ANA EMANDI

GENERAL CHEMISTRY

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I. Basic chemistry

I.1. Matter and energy

1.1 Matter

1.1.1 Introduction

Matter is anything that occupies space and has weight. Matter cannot be created or destroyed (Law of Conservation of Mass). Its shape can be altered.

A mixture is matter that contains materials of variable composition and properties. A compound or element is matter that contains materials of constant composition and properties.

1.1.2 States of Matter: Gas, Liquid or Solid

A change in temperature or pressure can usually change matter from one state to another. Transformations usually take place at definite temperatures and pressures. Melting or freezing points are the transition points of solids or liquids. Water freezes or ice melts at 0°C. Boiling point is the transition point of liquid or gas. Water boils at 100°C under a pressure of one atmosphere

1.1.3 Classification of Matter: Elements or Compounds

Elements:

An element is a simple substance that cannot be separated into simpler substances by ordinary chemical means. There are 103 known chemical elements from which all substances are derived by various combinations. Representative examples of chemical elements are iron, copper, aluminium, gold, silver, sulphur, oxygen and hydrogen.

Elements can be classified as metals or non-metals, although some possess the properties of both.

Properties of metals:

All metals, except mercury are solids. Metals show high electrical and thermal conductivity. Metals have high luster and they are non-transparent. Metals are usually ductile and malleable.

Properties of non-metals:

Non-metals show low electrical and thermal conductivity. Many non-0metals show moderate transparency. Non-metals, if solids, show marked brittleness and lack of ductility.

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Element	Composition of terrestrial matter in per cent				
	Solid crust of Earth	Oceans	Atmos-phere Sea level	Average of all	Relative number of atoms
Oxygen	41.17	85.69	21.0	50.02	54.87
Silicon	28.00	.....	.....	25.80	16.17
Aluminium	7.84	.....	.....	7.35	4.76
Iron	4.44	.....	.....	4.18	1.40
Calcium	3.42	0.05	.....	3.22	2.14
Sodium	2.43	1.14	.....	2.36	1.00
Potassium	2.49	0.04	.....	2.28	16.54
Magnesium	2.27	10.67	.....	2.02	
Hydrogen	0.23	2.07	0.01	0.95	
Chlorine	0.06	.....	.....		
Argon	.....	.....	0.9		
Carbon dioxide	.....	.....	0.03		
Helium	.....	.....	0.00015		
Neon	.....	.....	0.0015		
Nitrogen	.....	.....	78.0		
Others	1.65	0.10	0.05835	1.82	3.12

Average composition of oceanic salts from sea water:

Substance	Percentage
Sodium chloride, NaCl	77.76
Magnesium chloride, $MgCl_2$	10.88
Magnesium sulphate, $MgSO_4$	4.74
Calcium sulphate, $CaSO_4$	3.60
Potassium sulphate, K_2SO_4	2.46
Magnesium bromide, $MgBr_2$	0.22
Calcium carbonate, $CaCO_3$	0.34

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Elements of the human body:

Substances	Percentage
Oxygen	65.0
Carbon	18.0
Hydrogen	10.0
Nitrogen	3.0
Calcium	2.0
Phosphorous	1.0
Potassium	0.35
Sulphur	0.25
Sodium	0.15
Magnesium	0.05
Iron	0.004
Iodine	a trace
Fluorine	a trace
Silicon	a trace

Compounds

Chemical compounds are formed by chemical combinations of two or more different elements. These compounds in turn may be decomposed into their constituent elements by chemical means.

There are over 300000 known compounds. Chemical compounds are characterized by always having homogeneity, a constant composition, and definite chemical and physical properties.

Water is a compound substance, formed from hydrogen and oxygen. The properties of water are quite different from those of either of its constituent elements. Compounds may be variously classified as acids, bases, salts, oxides, etc.

1.1.4 Changes in matter

Physical changes in matter alter only the physical properties of a substance and not the chemical properties. The composition remains the same and the original properties can

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usually be restored by simple means. The original substance retains its identity. The freezing of water, the breaking of glass and the grinding of sugar are examples of physical change.

Chemical changes alter the properties, and particularly the chemical properties, so completely that there results an entire new substance. The burning of oil, the rusting of iron and the fermentation of fruit juices are examples of chemical change. There are fundamentally five types of chemical change:

(1) Chemical combination is the direct combination of two or more elements or compounds to form more complex compounds. Iron combines with oxygen to form iron rust.

(2) Decomposition is the breaking down of a compound into two or more simpler substances. Water decomposes into its constituent elements, hydrogen and oxygen by electrolysis.

(3) Displacement is when a free element displaces another element into a compound. An iron nail displaces copper from a solution of copper sulphate.

(4) Double decomposition is when two compounds react with each other to give two new compounds. Sodium hydroxide (household lye) reacts with hydrochloric acid (muriatic acid) to produce sodium chloride and water.

(5) Internal rearrangement is when the atoms within a molecule rearrange to give a different compound without the loss or gain of any atoms. Ammonia cyanate, when heated, produces urea.

1.1.5 Properties of matter: physical or chemical

Physical properties: color- sulphur is yellow, odor- ammonia is sharp odor, taste- sugar is sweet, specific gravity- lead is heavy, aluminium is light, hardness- chromium is hard, electrical conductivity- copper is high, heat conductivity- aluminium is high, melting point- carbon is extremely high, tensile strength- iron and steel are high, ductility- silver is unusually ductile, malleability- gold is unusually malleable.

Chemical properties:

-stability toward heat: quicklime, CaO, is stable toward heat while mercuric oxide, HgO, is easily decomposed with heat.

-resistance to reaction when brought into contact with other substances: iron rusts readily in contact with moist air while gold does not.

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I. 2 WEIGHT RELATIONS IN CHEMICAL CHANGE

2.1 Laws of chemical combinations

2.1.1 Law of Conservation of Mass

There is no detectable loss or gain of weight in any chemical change. No matter how completely the reacting substances may have their other chemical or physical properties altered, there is one property, their total weight, or total mass, which remains unchanged.

In some rare instances of nuclear transformations of one element into another there is a detectable alternations in mass, with a proportionate change in energy.

To demonstrate the validity of this law, two solutions, capable of reacting with each other, are sealed in the two separate arms of the tube. The whole is carefully weighed and then inverted to allow the contents to thoroughly mix and react. Regardless of the nature of the reaction, no detectable change in weight has ever been observed.

2.1.2 Law of Definite Proportions

The substances transformed or produced in any given chemical change have invariable weights, relative to another. That is, the weights transformed and produced, in comparison with one another, are fixed and invariable as long as the same reactants and resultants are concerned, e.g.

100g water →88.81g oxygen+11.19g hydrogen

88.81g oxygen+11.19g hydrogen→100g water

66.47g copper+33.53g sulphur →100g copper sulphide

Such exact rations for these and other reactions are always obtained. Thus it becomes obvious that every pure chemical compound always contains the same percentage of its constituent elements.

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2.1.3 Law of Multiple Proportions

When two elements combine in more than one proportion to form more than one compound, then the weight of the second element that combines with a fixed quantity of the first element is always in the ratio of small whole numbers.

E.g. 2g hydrogen + 16g oxygen→18g water

2g hydrogen + 32g oxygen →34g hydrogen peroxide

Ratio of oxygen is 16 to 32 or 2 to 1.

28g nitrogen + 48g oxygen →76g nitrogen trioxide ..

28g nitrogen + 80g oxygen →108g nitrogen pentoxide

Ratio of oxygen is 48 to 80 or 3 to5.

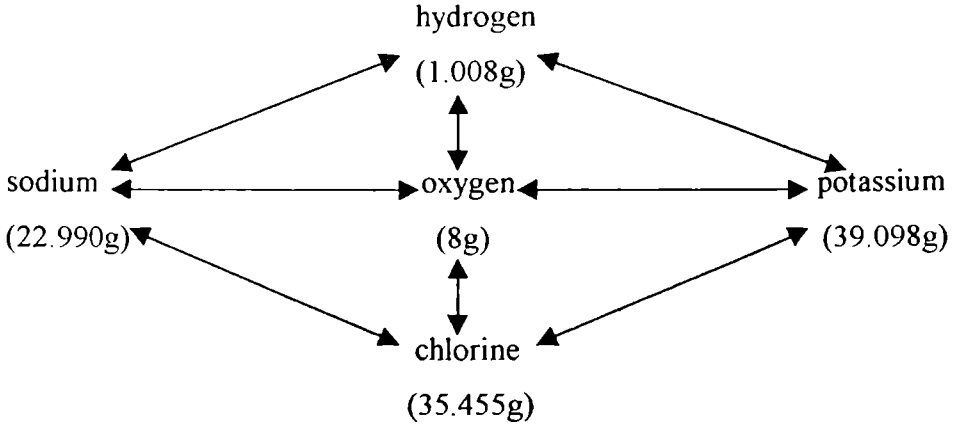
2.1.4 Law of Combining Weights

Each element may have assigned to it a characteristic number, or a simple multiple of that number, which will then represent the weight of that element which will combine with other elements.

Oxygen with a combining weight value of 8 is taken as the standard. The grams of any other element that combines with 8 grams of oxygen, or its equivalent, is the combining weight of that element.

8g of oxygen combines with 1.008g of hydrogen, 22.990g sodium, 39.098g potassium or 35.453g chlorine.

Likewise, 1.008g hydrogen combines with 22.990g sodium or 39.098g potassium; and 35.453g chlorine combines with 22.990g sodium or 39.098g potassium. Other similar combinations can be arranged.



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I.3 Symbols, formulae and equations

I.3.1 Symbols and formulae

Each element is represented by a symbol-either a capital letter alone or a capital letter and a small letter. The complete list of symbols can be reference to the Periodic Table.

Each compound is represented by a formula which gives the proportions of the different elements it contains. For example, 24 g of magnesium combines with 16 g of oxygen in every 40 g sample of magnesium oxide. The formula is MgO, showing that 1 mole of magnesium atoms (24 g) combines with 1 mole of oxygen atoms (16 g).

The formula of many compounds can be use of the list of ions in Table1.

Table 3.1 - Common ions

Positive ions	Negative ions
lithium Li^+	fluoride F^-
sodium Na^+	chloride Cl^-
potassium K^+	bromide Br^-
silver Ag^+	iodide I^-
copper(II) Cu^{2+}	hydroxide OH^-
lead(II) Pb^{2+}	nitrate NO_3^- (nitrate(V))
magnesium Mg^{2+}	nitrite NO_2^- (nitrate(III))
calcium Ca^{2+}	carbonate CO_3^{2-}
strontium Sr^{2+}	hydrogencarbonate HCO_3^-
barium Ba^{2+}	sulphate SO_4^{2-} (sulphate(VI))
zinc Zn^{2+}	hydrogensulphate HSO_4^-
aluminium Al^{3+}	sulphite SO_3^{2-} (sulphate(IV))
iron(II) Fe^{2+}	oxide O^{2-}
iron(III) Fe^{3+}	sulphide S^{2-}
chromium(III) Cr^{3+}	phosphate PO_4^{3-} (phosphate(V))
manganese(II) Mn^{2+}	manganate(VII) MnO_4^-
cobalt(II) Co^{2+}	ethanedioate $C_2O_4^{2-}$
nickel(II) Ni^{2+}	chlorate(V) ClO_3^-
ammonium NH_4^+	chlorate(I) OCl^-
hydrogen H^+	chromate(VI) CrO_4^{2-}
	dichromate(VI) $Cr_2O_7^{2-}$

In forming the compound, the number of ions used is such that the number of positive charges equals the number of negative charges. For example, sodium chloride is made up from

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Na^+ and Cl^- ions. Since a sodium ion has a single positive charge and chloride ion has a single negative charge, the formula of sodium chloride is NaCl. Sodium sulphate is made up from Na^+ and SO_4^{2-} ions. Twice as many sodium ions as sulphate ions are necessary in order to have equal positive numbers of positive and negative charges. The formula is Na_2SO_4. Chromium(III) sulphate is made up from Cr^{3+} and SO_4^{2-} ions and its formula is $Cr_2(SO_4)_3$. Table 3.2 contains further examples.

Table 3.2 Finding the formula

Compound	Ions present		Formula
copper(II) oxide	Cu^{2+}	O^{2-}	CuO
ammonium chloride	NH_4^+	SO_4^{2-}	$(NH_4)_2SO_4$
potassium manganate(VII)	K^+	MnO_4^-	$KMnO_4$
calcium ethanedioate	Ca^{2+}	$C_2O_4^{2-}$	CaC_2O_4
chromium(III) oxide	Cr^{3+}	O^{2-}	Cr_2O_3
hydrochloric acid	H^+	Cl^-	Hcl
nitric acid	H^+	NO_3^-	HNO_3
sulphuric acid	H^+	SO_4^{2-}	H_2SO_4

All of the compounds above are composed of ions. Many compounds are not ionised. The formulae of some of these compounds are shown in Table 3.

Table 3.3 Some compounds not composed of ions

Compound	Formula	Compound	Formula
Water	H_2O	Sulphur dioxide	SO_2
Carbon dioxide	CO_2	Sulphur(VI) oxide	SO_3
Carbon monoxide	CO	Ammonia	NH_3
Nitrogen monoxide	NO	Hydrogen chloride	HCl
Nitrogen dioxide	NO_2	Methane	CH_4

3.3 Chemical equations

Chemical equations are widely used in textbooks an examination papers. An equations is a useful summary of a chemical reaction, and it is always theoretically possible to obtain the

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equation from the results of an experiment. It is advisable to be able to write equations in your answers to A level questions. You should write any relevant equation even if you are not directly asked to do so.

The steps in writing a chemical equation are as follows:

(i) Write down the equation as a word equation using either the information given or your memory. Include all reacting substances (reactants) and all products (do not forget small molecules such as water) *e.g.*

calcium hydroxide + hydrochloric acid → calcium chloride + water

(ii) Fill in the correct formulae for all the reacting substances and products.

$$Ca(OH)_2 + HCl \rightarrow CaCl_2 + H_2O$$

(iii) Now balance the equations. During a chemical reaction, atoms cannot be created or destroyed (Law of conservation of mass). There must be the same total numbers of the different atoms before and after the reaction. When balancing an equation only the proportions of the reacting substances and products can be altered-not the formulae.

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$

In organic chemistry the equations can be more complex. Frequently, in the interest of clarity, the formulae are drawn out as structural formulae to show clearly the changes that have taken place. Also, less emphasis may be given to balancing the equation. You should however balance the equation if possible.

For example, the reaction between bromoethane and a solution of potassium hydroxide in ethanol can be written.

$$CH_3CH_2Br \xrightarrow{-HBr} C_2H_4$$

It is better to write

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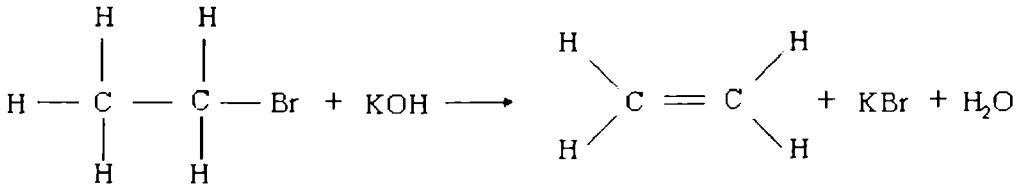

The equation is balanced and shows clearly the change taking place *i.e.* elimination of HBr.

(iv) Finally, the states of reacting substances and products can be included in small brackets after the formulae.

(s) for solid (sometimes (c) is seen for crystaline solid)

(l) for liquid

(g) for gas

(aq) for a solution with water as solvent

These state symbols may not be required and may not give you extra credit from the examiner but they do help your thinking considerably and give a good impression.

$$Ca(OH)_2\,(aq) + 2HCl\,(aq) \rightarrow CaCl_2\,(aq) + 2H_2O\,(l)$$

In the interests of simplicity of this text, state symbols are not included throughout the book, unless considered important.

3.4 Information provided by an equation

$$CaCO_3\,(s) + 2HCl\,(aq) \rightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

This equation gives the following information: 1 mole of calcium carbonate reacts with 2 moles of hydrochloric acid to produce 1 mole of calcium chloride, 1 mole of carbon dioxide and 1 mole of water. The equation also gives the states of all reactants and products.

In general, a chemical equation gives:

(i) the chemicals reacting together and the chemicals produced,

(ii) the physical states of reactants and products, and

(iii) the quantities of chemicals reacting together and produced.

The equation does not, however, give information about energy changes, the feasibility of reaction, the rate of reaction or the conditions necessary for reaction to take place.

At O level you will have attempted calculations of quantities of chemicals reacting. For example, using the above equation and the relative atomic masses (H = 1, C = 12, O = 16, Cl =

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35.5, Ca = 40), calculate the mass of solid calcium chloride which could be produced from 20g of calcium carbonate.

From the equation, 1 mole of calcium carbonate ($CaCO_3$) produces 1 mole of calcium chloride ($CaCl_2$)

$40 + 12 + (3 \times 16)$g $CaCO_3$ produces $40 + (35.5 \times 2)$g $CaCl_2$

100g $CaCO_3$ produces 111g $CaCl_2$

$$20\text{g } CaCO_3 \text{ produces } \frac{111}{100} \times 20\text{g } CaCl_2$$

$$= 22.2\text{g of } CaCl_2$$

You will attempt similar questions at A level. In some cases, for example when considering carbon dioxide as a product, it is more usefull to measure the volume of gas produced. This can then be converted into numbers of moles of carbon dioxide by using the information (given on the examination paper) that 1 mole of any gas occupies 22 400 cm^3 at standard temperature and pressure, stp. If the volume is measured at conditions other than stp, and it usually is, it is necessary to convert the volume measured to the volume the gas would occupy at stp (273 K and 101.3 kPa) using the equation:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

For example, what mass of calcium carbonate would react with dilute hydrochloric acid to produce 133.5 cm^3 of carbon dioxide at 27°C and 100 kPa.

Volume of carbon dioxide at stp = V_1 cm^3

$$\frac{V_1 \times 101.3}{273} = \frac{133.5 \times 100}{(273 + 27)}$$

$$V_1 = \frac{133.5 \times 100 \times 273}{101.3 \times 300} = 120\ cm^3$$

From the equation,

100g of calcium carbonate (1 mole) produces 22 400 cm^3 CO_2 at stp

$\frac{100 \times 120}{22400}$ g of calcium carbonate produces 120 cm^3 CO_2 at stp

Mass of calcium carbonate = 0.54g

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3.5 Calculation of percentage yield

In organic chemistry, a 100% conversion of reactants into products is rarely achieved. From an equation it is possible to calculate a theoretical yield, *i.e.* the mass that would be produced if a 100% conversion were achieved. If you are given the actual mass produced, it is possible to calculate the percentage yield by:

$$\text{Percentage yield} = \frac{\text{mass obtained}}{\text{theoretical yield}} \times 100$$

Example: Propan-2-ol reacts with iodine and sodium hydroxide on warming to produce triiodomethane. In an experiment a student obtained 39g of triiodomethane from 10g of propan-2-ol. What was the percentage yield? (H = 1, C = 12, O = 16, Na = 23, I = 127).

$$CH_3CH(OH)CH_3 + 4\ I_2 + 6\ NaOH \rightarrow CHI_3 + CH_3COONa + 5\ NaI + 5\ H_2O$$

Mass of 1 mole of propan-2-ol = $(12 \times 3) + 8 + 16g = 60g$

Mass of 1 mole of triiodomethane = $12 + 1 + (3 \times 127) = 394g$

From 60g of propan-2-ol, 394g of triiodomethane would be produced if 100% conversion.

$$\text{Theoretical mass of triiodomethane from 10g propan-2-ol} = \frac{394}{6}\text{g} = 65.66\text{g}$$

$$\text{Percentage yield} = \frac{39}{65.66} \times 100 = 59.4\%$$

3.6 Ionic equations

You may well have written ionic equation at O level but they become much more significant at A level. Ionic equations are usefull because they emphasise the important changes taking place in a chemical reaction.

Taking the reaction between acidified potassium manganate (VII) and iron (II) sulphate as an example. The full equation is:

$$2\ KMnO_4 + 8\ H_2SO_4 + 10\ FeSO_4 \rightarrow 2\ MnSO_4 + 8\ H_2O + 5\ Fe_2(SO_4)_3 + K_2SO_4$$

In this equation there are a number of ions which take no part in the chemistry; they are present before and after the reaction. These tend to confuse the change taking place and can often be ignored.

Expanding the equation to show the ions present.

$$2(K^+MnO_4^-) + 8(2H^+SO_4^{2-}) + 10(Fe^{2+}SO_4^{2-}) \rightarrow 2(Mn^{2+}SO_4^{2-}) + 8H_2O + 5(2Fe^{3+}3SO_4^{2-}) + 2K^+SO_4^{2-}$$

Cross out ions appearing on both sides of equation

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \rightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

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The equation can be divided through by 2 to give the simplest equation.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

The represents the simplest ionic equation for this reaction. The equation must be balanced in the usual way with equal numbers of each type of atom on left and right hand sides. In addition, the algebraic sum of the charges on the left hand side equals that of the right hand side.

In the example,

$$LHS\ (-) + 8(+) + 5(2+) = 17(+)$$

$$RHS\ (2+) + 4(0) + 5(3+) = 17(+)$$

The ionic equation can be broken down into 2 half equations which added together produce the overall equation.

(i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

(ii) $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

Equation *(i)* represents the equation of mangahese(VII) to manganese(II). Equation *(ii)* represents the oxidation of iron(II) to iron(III).

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II. Development of the atomic theory

II.1. Atomic and molecular theory

1.1 Introduction

Molecules are the smallest ultimate particles that compose all larger samples of the same kind of matter and determine their properties.

All molecules of a pure substance are alike, but different from the molecules of all other substances. Matter is composed of a limited number of elementary substances. Molecules are in turn composed of the same limited number of still smaller particles called atoms. There are as many chemically distinct kinds of atoms as there are chemically distinct elementary substances.

An atom is the smallest particle of an element that can unite with particles of other elements to form molecules of a compound.

1.2. **The atomic theory** (proposed by John Dalton in 1804)

Every element is composed of very small particles called atoms. The atoms of the same element are practically all alike. Isotopes constitute an exception. They have a constant average weight. The atoms of one element are different from the atoms of every other element. The atoms of different elements combine chemically to form the molecules of the compounds. The atoms have definite, fixed and unchangeable weights. The atoms are indestructible. Recent developments have enabled us to alter some few types of atoms.

1.3. The molecular theory

Matter is ultimately formed from molecules. Molecules in turn are formed from one or more atoms. All molecules of the same pure substances are alike. Molecules of different substances are different. The mass of a molecule is the sum of the masses of the atoms that compose the molecule (molecular weight). A molecule is the smallest particle that still retains the properties of the original substance.

1.4. Applications of the atomic and molecular theory

Law of conservation of mass:

During any chemical reaction the atoms within the molecule separate, combine or rearrange without the creation or destruction of any atoms originally present. There is, therefore, no loss or gain in total weight of mass.

Law of definite proportions:

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Molecules of the same pure substance always contain the same number and arrangement of individual atoms within each molecule. They, therefore, combine or decompose in the same ratio and the resulting compounds always have the same percentage composition.

Law of multiple proportions:

Two atoms of hydrogen combine with one atom of oxygen to form water, but two atoms of hydrogen combines with two atoms of oxygen to form hydrogen peroxide. One atom of carbon combines with one atom of oxygen to form carbon monoxide, but one atom of carbon combines with two atoms of oxygen to form carbon dioxide. Two atoms of nitrogen combines with three atoms of oxygen to form nitrogen trioxide, but two atoms of nitrogen combine with five atoms of oxygen to form nitrogen pentoxide.

Law of combining weights:

Since the atoms of every individual element have a constant average weight it is possible to assign a characteristic weight of the atoms of each elementary substance. This weight is called the atomic weight. The atomic weights of the elements combined and the number of atoms of each kind combined will determine the combining weights. Hydrogen with an atomic weight of 1.008 combines atom for atom with sodium with an atomic weight of 22.990. Hence, their atomic weights and their combining weights are the same.

The molecules that compose liquids and solids may slip or roll past one another. The salt molecules enter the openings between the water molecules. The molecules are separated from one another, when a substance is heated.

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II.2. Atomic structure

2.1. Introduction

Atoms are composed of protons, neutrons and electrons Table 1.1 compares the properties of these three particles.

Table 1.1 Particles in an atom

Name of particle	Mass	Charge
proton p	1 a.m.u.*	+1
neutron n	1 a.m.u.	0
electron e	negligible	-1

*a.m.u.- atomic mass unit

An atom is neutral and contains equal numbers of protons and electrons.

Atomic number (Z)- the number of protons in an atom

Mass number (A)- the total numbers of protons and neutrons in an atom.

E.g. $^{39}_{19}K$ represents a potassium atom with mass number 39 and atomic number 19

The number of protons, neutrons and electrons in potassium atom is 19,20 (i.e. 39 - 19) and 19 respectively. It is possible to get other potassium atoms, namely . ^{40}K and ^{41}K containing the same number of protons and electrons (19) but different number of neutrons (21 and 22) .These different atoms of the same element are called isotopes. A sample of potassium contains 93.1% potassium-39, 0.012% potassium-40 and 6.9% potassium -41.

The **relative atomic mass** (represented by A_r) is a mass of an atom based on a scale such that the $_6{}^{12}C$ isotope has a mass of 12.00 units.

$$\text{relative atomic mass} = \frac{\text{mass of 1 atom of element} \times 12}{\text{mass of 1 atom of carbon-12}}$$

2.2 Evidence for protons, neutrons and electrons

Electrons

J.J. Thompson discovered that a beam of rays was emitted from the cathode when an electric discharge was passed through a gas at a very low pressure. These rays were deflected by a magnetic field and behaved in the same way whichever gas was used. These ray consist of streams of **electrons**.

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Protons

The passage of an electric discharge at very low pressures also produces a stream of particles from the anode. These particles were obtained when hydrogen was the gas used and these particles were assumed to be **protons**.

Neutrons

The neutron was more difficult to characterise than the electron or proton. Chadwick (1932) bombarded the element beryllium with α (alpha) particles and noticed that fast moving, highly penetrating particles were produced. These particles, now known to be **neutrons**, were not deflected by electric or magnetic fields. The following equation summarises the change taking place.

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He (alpha particle)} \rightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

2.3. The nucleus

The protons and neutrons in each atom are tightly packed in a positively charged **nucleus** and the electrons move around the nucleus. In chemical reactions the nucleus remains unchanged.

Radioactivity is the breaking down of the nucleus with the emission of a α, β or γ rays. Radioactivity results in the formation of a new element.

Geiger and Marsden bombarded a thin gold foil with a beam of α particles. Most of the particles passed through the foil without deflection and were detected by a flash of light when the α particle struck a zinc sulphide screen. A few were deflected and some of these were deflected at angles greater than 90° suggesting they had been repelled by large positive charges within the foil-nuclei of atoms of gold.

2.4. Arrangement of electrons around the nucleus

The electrons are in certain **energy levels** and each energy level can hold only up to a certain maximum number of electrons. This is summarised in Table 1.2.

Table 1.2 Energy levels

Energy level or shell	*Maximum number of electrons*

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1st or K shell	2
2nd or L shell	8
3rd or M shell	18
4th or N shell	32
5th or O shell etc.	50

A sodium atom containing 11 electrons has an electronic arrangement of 2,8,1 -the 1st and 2nd shells being full. This is sometimes represented in a simple Bohr diagram (Fig.).

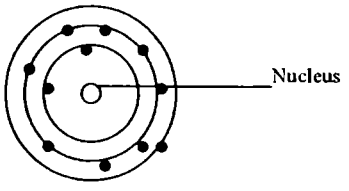
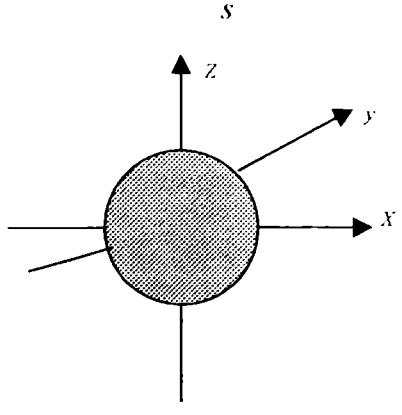


Fig. Simple representation of sodium atom

It has been found, by spectroscopic means, that all the electrons in the 2nd energy level are not exactly identical in energy. It is possible to break down this energy level into sub shells.

Electrons, partly because of their very small size, are impossible to locate exactly at any particular time. It is however possible to indicate a region or volume where the electron is most likely to be. This region is called an **orbital.** Each orbital is capable of holding a maximum of two electrons. Orbitals can be divided into *s*, *p*, *d* and *f* types. Each type has it's own characteristic shape. The shapes of *s* and *p* orbitals are shown in Fig. but it should be remembered that these orbitals are not flat but are three-dimensional.



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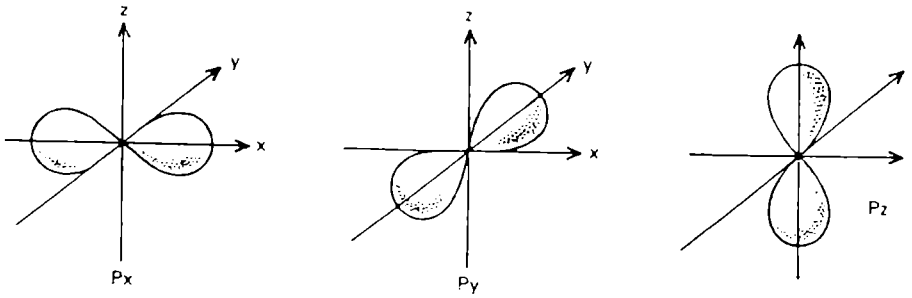


Fig. 1.2 The *s* and *p* orbitals

The first energy level holds a maximum of two electrons in one *s*-type orbital (called 1*s*). There are no *p*, *d* or *f* orbitals available.

The second energy level consists of one *s* type orbital and three types of *p* orbitals -2*s*, $2p_x$, $2p_y$, $2p_z$.

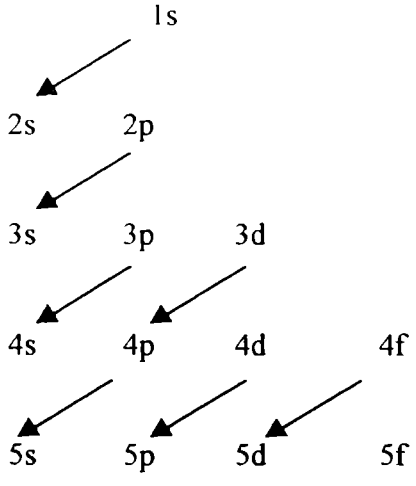
Note: there are three *p* orbitals of identical energy -one along of the x axis, one along of the y axis and one along of the z axis.

These four orbitals can hold a total of eight electrons (*i.e.* 2 electrons- each). There are no 2*d* and 2*f* orbitals.

The third energy level consists of one *s* type orbital, three p type orbitals and five d type orbital. These nine orbitals can hold a maximum of 18 electrons altogether (two electrons each).

When filling the available orbitals with electrons two important principles should be remembered:

(i) Electrons fill the lowest energy orbitals first and other orbitals in order of ascending energy.. It is incorrect to assume that an energy level is always completely filled before electrons enter the next energy level. The order of filling orbitals is shown in Fig 1.3.



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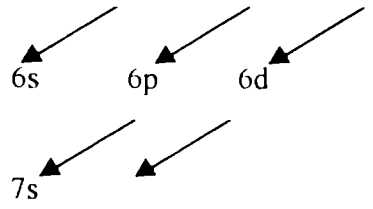

Fig. The order of filling orbitals

The order of filling orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p.

(ii) Where there are several orbitals of exactly the same energy (e.g. three 2p orbitals), electrons will occupy different orbitals wherever possible (e.g. nitrogen is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ and not $1s^2 2s^2 2p_x^2 2p_y^1$. When an orbital only contains one electron then this electron is called **unpaired .** This principle is called **Hund's rule**.

Table summarises the electron arrangements of the first 20 elements. For comparison the simple O level electrons are given.

Table Electron arrangement of the first 20 elements

Element	*O level*	*A level*
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Lithium	2,1	$1s^2 2s^1$
Beryllium	2,2	$1s^2 2s^2$
Boron	2,3	$1s^2 2s^2 2p_x^1$
Carbon	2,4	$1s^2 2s^2 2p_x^1 2p_y^1$
Nitrogen	2,5	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
Oxygen	2,6	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
Fluorine	2,7	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
Neon	2,8	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$
Sodium	2, 8, 1	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^1$
Magnesium	2, 8, 2	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2$
Aluminium	2, 8, 3	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1$
Silicon	2, 8, 4	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1 3p_y^1$
Phosphorus	2, 8, 5	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1 3p_y^1 3p_z^1$
Sulphur	2, 8, 6	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^1 3p_z^1$
Chlorine	2, 8, 7	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^1$
Argon	2, 8, 8	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^2$
Potassium	2, 8, 8, 1	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^2 4s^1$
Calcium	2, 8, 8, 2	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^2 3p_z^2 4s^2$

Note: Sometimes electronic structures are shown in a slightly condensed for e.g. Calcium $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

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Note on table

(i) The small number above the orbital refers to the number of electrons in the orbital e.g. $1s^2$ means two electrons in a 1s orbital.

(ii) The noble gases (helium, neon, argon, krypton, radon and xenon) contain filled s and, in all cases except helium, completely filled p orbitals. This s^2p^6 electron arrangement is very difficult to break down.

(iii) The electronic arrangements are sometimes abbreviated. For example, the electronic arrangement of calcium may be written as $1s^22s^22p^63s^23p^64s^2$. It is important to remember, however, that the six electrons in 2p and 3p orbitals are in three separate orbitals each holding two electrons.

2.5. Mass spectrometer

The mass spectrometer (Fig. 1.4) is an instrument used for accurately measuring atomic mass and for finding the number of isotopes of an element present. The sample being tested is introduced into the instrument and is then ionised by heating, electrical discharge or electron bombardment. The ions produced are accelerated and passed through a slit to give a fine beam of ions all moving with the same velocity. The individual ions in the beam will differ slightly in mass and charge. The beam of ions is then subjected to a magnetic field, which bends the beam into a circular path. Depending upon the mass and charge, the radius of the circular path for each ion is slightly different. The lighter the ion or the greater the charge on the ion the greater will be the deflection. The ions are detected of the means of photographic plate.

If neon is used as the sample the results are shown in Fig. 1.5. There are two sets of three lines . One set corresponds to the formation of Ne^+ ions in spectrometer by the loss of one electron from each atom. The other set corresponds to the formation of Ne^{2+} ions by the loss of two electrons. There are three lines in each group because neon consists of three isotopes-neon-20, neon-21 and neon-22. From the intensities it is possible to work out the relative abundance of the three isotopes. The spectrometer can be calibrated by the use of carbon-12.

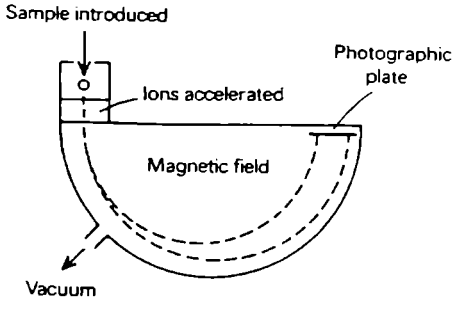

Fig. 1.4 Mass spectrometer

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Fig. The mass spectrum of neon

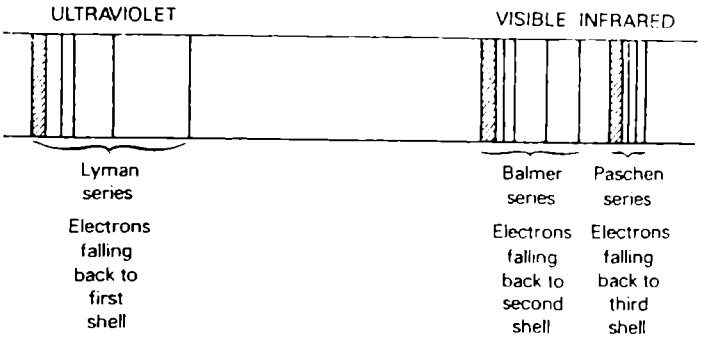

Fig. 1.6 The emission spectrum of the hydrogen atom

2.6. Atomic spectrum of hydrogen

When an electrical discharged is passed through a sample of hydrogen gas at low pressure, a pinkish glow is observed. This glow can be examined using a simple spectroscope-a number of separate lines can be observed and there are also lines in the ultraviolet and infrared regions (Fig. 1.6).

Lines in the spectrum correspond to electronic changes within the atoms. The fact that only certain lines are observed indicates that only certain energy changes are possible and this is evidence for the existence of distinct energy levels within the hydrogen atom.

When the electrical discharge is passed through hydrogen gas, energy is absorbed and the electron in the first energy level is promoted to a higher energy level. This electron may then drop back into a lower energy level giving out energy in the form of electromagnetic radiation of a definite frequency. This energy change is related to the frequency of the radiation by the formula

$$\Delta E = h\nu$$

where ΔE is the energy change

h is a constant (Planck's constant)

ν is the frequency of the radiation (light etc.)

It is important to realise that each line in the spectrum corresponds to a transition between the separate energy levels .

When the electron drops back into the first energy level this results in one of the lines in the **Lyman series**. The **Balmer series** corresponds to falling back into the second shell from a higher shell, while **Paschen series** corresponds to electrons falling back to the third shell.

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III. ELECTRONS IN ATOMS

III.1 The Aufbau Principle

Configurations of Many-electron Atoms

By the term configuration of an atom, we mean the distribution of electrons among the various orbitals. The aufbau principle (German *Aufbau*, "building up") is used to deduce the electronic configurations of multielectron atoms by building them up, that is, by adding protons and electrons to the hydrogen atom. In its simplest form the aufbau principle states that we should place the electrons of a multielectron atom in a set of orbitals formally the same as those for hydrogen, filling them in the order of decreasing stability and taking account of the exclusion principle. The order of energies of the orbitals in multielectron atoms is somewhat the same as the order for the hydrogen orbitals, but differences, to be discussed below, do occur. In assuming that the multielectron atom has a set of orbitals corresponding to the hydrogen orbitals, we are really assuming that one electron does not interact with the order electrons, but acts as through it were the only electron there. This is a satisfactory assumption except that each electron will tend to modify the effect which the electrostatic field of the nucleus has on each of the other electrons.

The ground state of the hydrogen atoM can be specified as 1*s*, meaning that the single electron occupies a 1*s* orbital. In this case we need not specify the spin of this electron since it has no effect on the energy, and we need not consider the exclusion principle since there is only one electron. Actually in a large number of hydrogen atoms in free space, half of the m_s values would be $+\frac{1}{2}$ and half of them $-\frac{1}{2}$. The next element in order of increasing atomic number is helium with two electrons. Its electronic structure is worked out as follows. If we start with the nucleus, He^{2+}, and add one electron we have a hydrogen-like atom, He^{+}, and the electron will occupy the 1*s* orbital. It can be assigned the quantum numbers $n = 1$, $l = 0$, $m_l = 0$, $m_s = \frac{1}{2}$, where the choice of $+\frac{1}{2}$ for m_s is arbitrary. Now, where will the second electron go in the process $He^{+} + e = He$? The 1*s* orbital is still the most stable one so that the electron will go into it since this can be done without violating the exclusion principle. This second electron has the quantum numbers $n = 1$, $l = 0$, $m_l = 0$, $m_s = -\frac{1}{2}$. This set differs from the first only in the spin, so that both electrons in the helium atom in its ground state are 1*s* electrons. This electron configuration is symbolized $1s^2$, the

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superscript indicating the number of electrons of the type specified. The spins of the two electrons are said to be paired. The atom is not paramagnetic.

With the configuration $1s^2$ the first principal shell is filled. Thus, when we come to lithium with three electrons, the first two go in to give Li^+ the configurations $1s^2$, but the remaining electron will have to enter the next most stable orbital, namely, $2s$ Thus the electronic configuration of Li is $1s^22s$. It has already been noted that in the hydrogen atom the energies of the orbitals increase with increasing n. While in the hydrogen atom there is no energy difference between an ns and an np level, there is a difference decidedly in favor of the ns level in all multielectron atoms. That is why the third electron of Li has been assigned as $2s$ rather than $2p$. The beryllium atom, which has four electrons, has the configuration $1s^22s^2$, and all electron spins are paired. When we reach boron, which has five electrons, the configuration must be $1s^22s^22p$, and there is one unpaired spin due to the $2p$ electron.

When we come next to carbon, which has six electr ons, we can easily enough decide that the electron configuration of its ground state must be $1s^22s^22p^2$, but we have as yet no basis deciding whether the spins of the two $2p$ electrons will be paired or unpaired. Pairing is not required by the exclusion principle since the two electrons which have $n = 2$, $l = 1$ can have the same spin and differ in their m_l values. The answer to this question is provided by a rule-of-thumb called Hund's first rule, which we shall discuss more fully later. For the present, we can state the import of this rule in a form particularly suitable for present purposes, viz., so long as the exclusion principle permits, electrons with the same n and l values will also have the same m_s values, thus, necessarly, occupying orbitals with different m_l values. Thus, for carbon the particular $1s^22s^22p^2$ configuration which occurs is that in which the two p orbitals are different, and the atom has paramagnetism corresponding to two unpaired electron spins. Similarly, for nitrogen the configuration is $1s^22s^22p^3$, and the p electrons are spread out among the three $2p$ orbitals with identical m_s values.

At oxyden we add a fourth $2p$ electron and this must enter a $2p$ orbital already occupied. Its n, l and m_l quantum numbers will then be identical with those of the electron already ocupying this orbital, so these two electrons must have their spins opposed. Thus in the oxygen atom there is a paramagnetism corresponding to two unpaired spins. In fluorine the configuration is $1s^22s^22p^5$, and there is only one unpaired electron spin. Neon has the configuration $1s^22s^22p^6$ and is not paramagnetic. At this point all orbitals in the first and second principal shells are filled.

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As in hydrogen, the next most stable orbitals after the $2s$ and $2p$ levels are the $3s$ and $3p$ orbitals. Consequently, beginning with sodium, Z = 11, and going through to argon, Z = 18, eight electrons are added in a manner quite analogous to the filling of the second shell. Beyond this, however, the pattern of levels deviates further from that for hydrogen. We might have expected that potassium, with Z = 19, would have the configuration [Ar]$3d$, where [Ar] represents a core with the configuration of argon, that is, $1s^2 2s^2 2p^6 3s^2 3p^6$. Actually the configuration of potassium is [Ar]$4s$. In order to understand this deviation from the hydrogen pattern as well as the general rule that $E_{ns} < E_{np}$, let us pause to consider in more detail the assumption implicit in the aufbau principle, namely, that a multi-electron atom ought to have a set of orbitals formally similar to those for a one-electron atom like hydrogen.

In a hydrogen or hydrogen-like atom the energy of an electron in a particular orbital depends only on the quantity Z/n^2, or, for a particular atom, on the quantum number n. Thus, for example, the $3s$, $3p$ and $3d$ orbitals should all have the same energy. An electron in one of these orbitals in hydrogen feels the presence of exactly one positive charge at the nucleus. Now, in the sodium atom an electron in, say, the $3s$ orbital feels a greater nuclear charge. If the $3s$ electron spent all of its time in regions completely ouside of that occupied by the electrons of the neon core, then the charge of + 11 on the nucleus would be shielded by the charge of - 10 of the neon core, and the $3s$ electron would feel a net nuclear charge of exactly + 1. However, this is not the case because the $3s$ wave function has a finite value even at the nucleus where it is subject to the full nuclear charge.

The $3s$ electron in sodium *penetrates* the neon core. Rather than being perfectly shielded so that the *effective nuclear charge*, Z^*, would be 1.0, it is, in fact, imperfectly shielded so that the effective nuclear charge is ~ 2. Now, the $3p$ orbital is also partly penetrating but not as much as the $3s$ orbital; consequently, it feels an effective nuclear charge between 1 and 2. The $3d$ orbital is practically nonpenetrating, and Z^* for it is very nearly 1.0. Thus, when the neon core is complete, there are appreciable differences in the energies of these orbitals such that the order of stability is $3s$, $3p$, $3d$.

In the region of argon and potassium in the sequence of elements, the shielding effects of inner, filled orbitals are such that the $4s$ orbital is less shielded than the $3d$ orbitals and hence more stable, whereas the $4p$ orbitals are not only more shielded than the $4s$, as usual, but also more

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shielded than the $3d$ orbitals. Thus the order of energies is $3s$, $3p$, $4s$, $3d$, $4p$. Similarly, following $4p$, the $5s$ orbital is more stable than $4d$. Now, in the fourth principal shell we have the first set of f orbitals.

These do not, however, follow the $4d$ orbitals. Instead, again mainly because of differences in the degrees of penetration of the core, they are less stable than the $5p$ and $6s$ orbitals. The complete list of the orbitals for neutral atoms, in the order in which they are filled is: $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, $4d$, $5p$, $6s$, $4f$, $5d$, $6p$, $7s$, $6d \sim 5f$.....

The electronic structures of most of the remaining atoms which are known can be worked out using this order and the principles discussed above. There are certain minor anomalies which will be discussed at appropriate places in the text. A complete list of the elements and their ground state electron configurations is given inside the front cover.

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III.2. Periodicity and the periodic table

2.1 Introduction

The way that properties change into the Periodic Table is called periodicity.

2.2. The Periodic Table

The Periodic Table is an arrangement of all chemical elements in order of increasing atomic number-elements with similar properties (i.e. the same chemical family) are placed in the same vertical column.

The Periodic Table was devided in 1869 by Mendeléef. at this time a number of elements that we know had not been discovered, but Mendeléef left gaps in his table and even predicted the properties of some of these undiscovered elements. Fig. 2.1 shows the modern Periodic Table.

The main difference between Mendeléef's table and the modern table, apart from the extra elements, is that the later arranges the elements in order of increasing atomic number rather then atomic mass.

The vertical columns are called **Groups**. A Group contains elements with similar properties and similar outer electronic arrangements. The Groups are given Roman numbers-e.g. Group IV. The elements in the alkali metal family (Group I) all have a single electron in the highest energy level .

The outer electron arrangements of elements in the different Groups are shown in Table 6.1

Table 6.1 Arrangements of outer electrons

Group	Outer electron arrangement
I	s^1
II	s^2
III	s^2p^1
IV	s^2p^2
V	s^2p^3
VI	s^2p^4
VII	s^2p^5
0	s^2p^{6*}

*Helium (the first element in group 0 has an electronic arrangement of $1s^2$

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The horizontal rows in the Periodic Tables are called **Periods**.

The elements shaded in Fig. 2.1 are called the s-block and p-block elements. The elements between the two shaded portions are called the d-block or transition elements. The two rows of elements at the bottom of the table are called f-block elements.

The bold line in Fig. 2.1 is an attempt to divide elements into metals and non metals. Elements on the right hand side of this line are non metals and on the left hand side are metals; but elements close to the line often show both metallic and non metallic properties, particularly if they exist in allotropic (polymorphic) forms.

2.3. Trends within the Periodic Table

Physical properties such as **ionisation energy, electron affinity, melting** and **boiling points** are related to electron arrangements. If one of these properties is plotted on the graph for each element, e.g. a graph of the property against atomic number, the graph has a characteristic shape. The shape consists of a series of peaks and troughs. An example is shown in Fig. 6.2.

You will notice that the element at the top of each peak is a noble gas (Group 0) and the element at the bottom is an alkali metal (Group I). Elements in the same Group are found to occur at similar positions on the different peaks.

In the following sections some of these physical properties will be discussed in greater detail.

2.4. Ionisation Energy (Ionisation Potential)

Ionisation energy is the energy absorbed when a mole of electrons is removed from a mole of atoms of an element in gaseous state to form a mole of positively charged ions.

i.e. $M(g) \rightarrow M^{+}(g) + e^{-}$

This is the **first ionisation energy**. The energy is usually quoted in units of kilojoules per mole ($kj\ mol^{-1}$). Energy is required to remove an electron from any atom because there is an attractive force between the nucleus and the electron being removed which has to be overcome. The value of the first ionisation energy depends upon:

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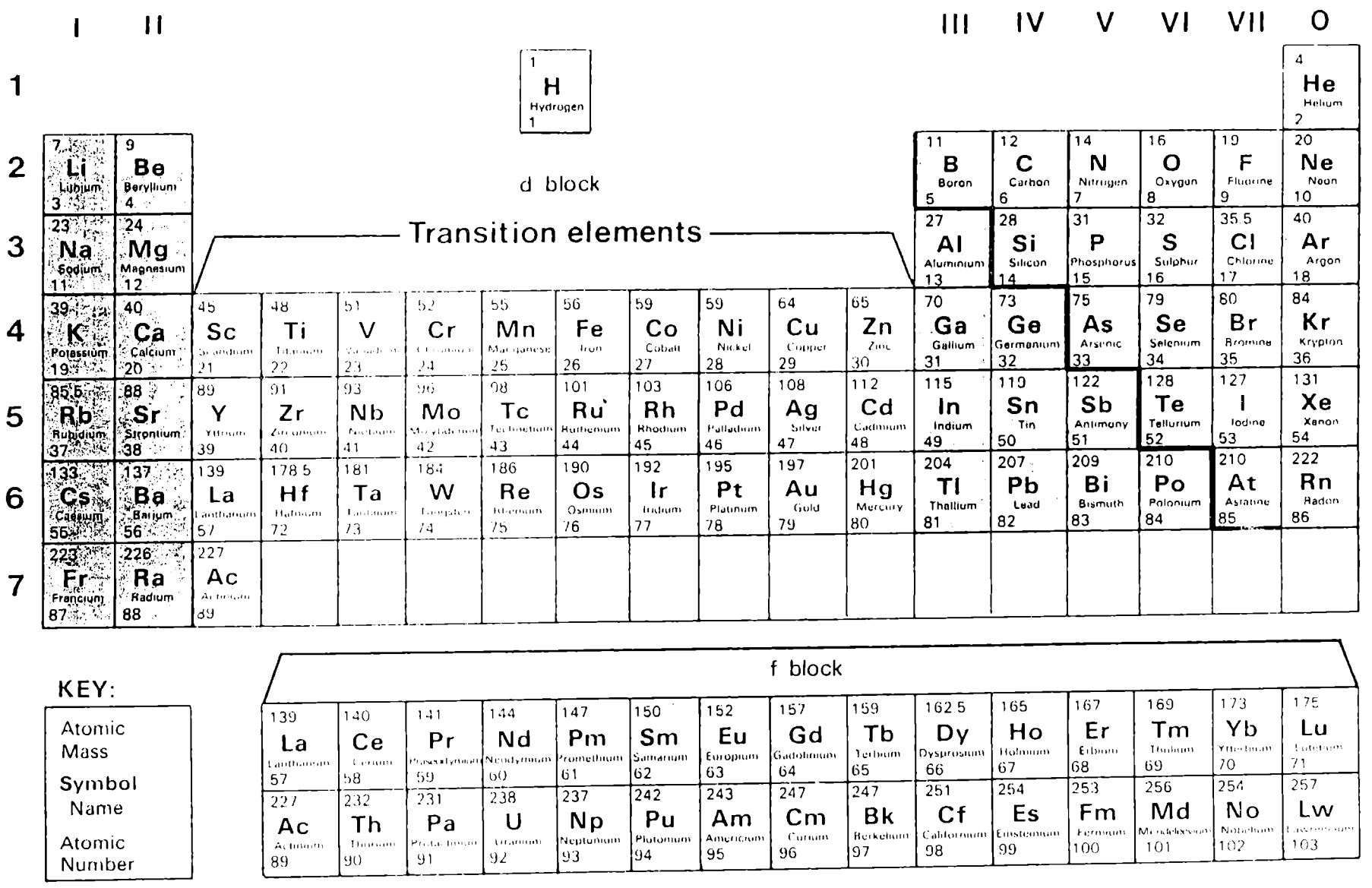

Fig. 2.1 The Periodic Table of elements

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(i) the effective nuclear charge,

(ii) the distance between the electron and the nucleus, and

(iii) the 'shielding' produced by lower energy orbitals.

Shielding involves the repulsion between electrons in inner filled orbitals and the electron being removed from the outer orbital.

Fig. 2.3 shows the variation of the first ionisation energy within the second and third Periods. Across each Period then is an increase in ionisation energy.

Beryllium (Group II) has an extra electron and proton compared with lithium. The extra electron goes into the same 2s orbitals. The increase in ionisation energy here can be attributed to the increased nuclear charge. The two breaks in the graphs (Be→B and N→O in the second period) can be explained by the increased shielding produced by full orbitals. The ionisation energy of boron is less than that of beryllium because, in boron there is a complete $2s^2$ orbital. The increased shielding of 2s orbital reduces the ionisation energy. Similarly, the ionisation energy of oxygen is less than that of nitrogen because the extra electron in oxygen is shielded by the half filled 2p orbitals.

Within a Group the first ionisation energy decreases down the Group as the outer electron becomes progressively further from the nucleus. Also, there is more shielding because of the extra filled orbitals.

E.g. for group I the first ionisation energies are:

Li 520 kj mol^{-1} Na 500 kj mol^{-1} K 420 kj mol^{-1} Rb 400 kj mol^{-1} Cs 380 kj mol^{-1}

The energy required to remove three electrons is not three times the energy required to remove one electron. The values for successive ionisation energies are related to electronic structures.

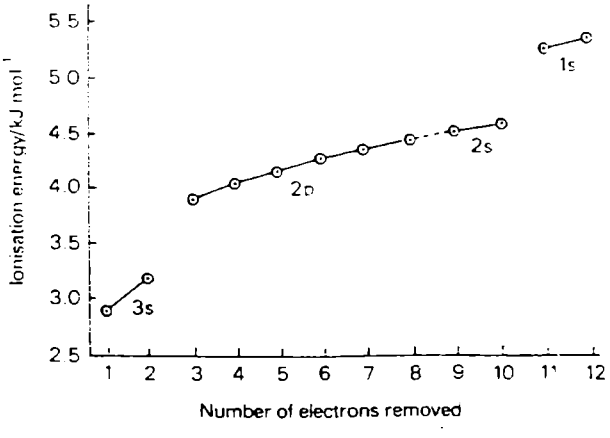

Fig. 4 Successive ionisation energies of magnesium

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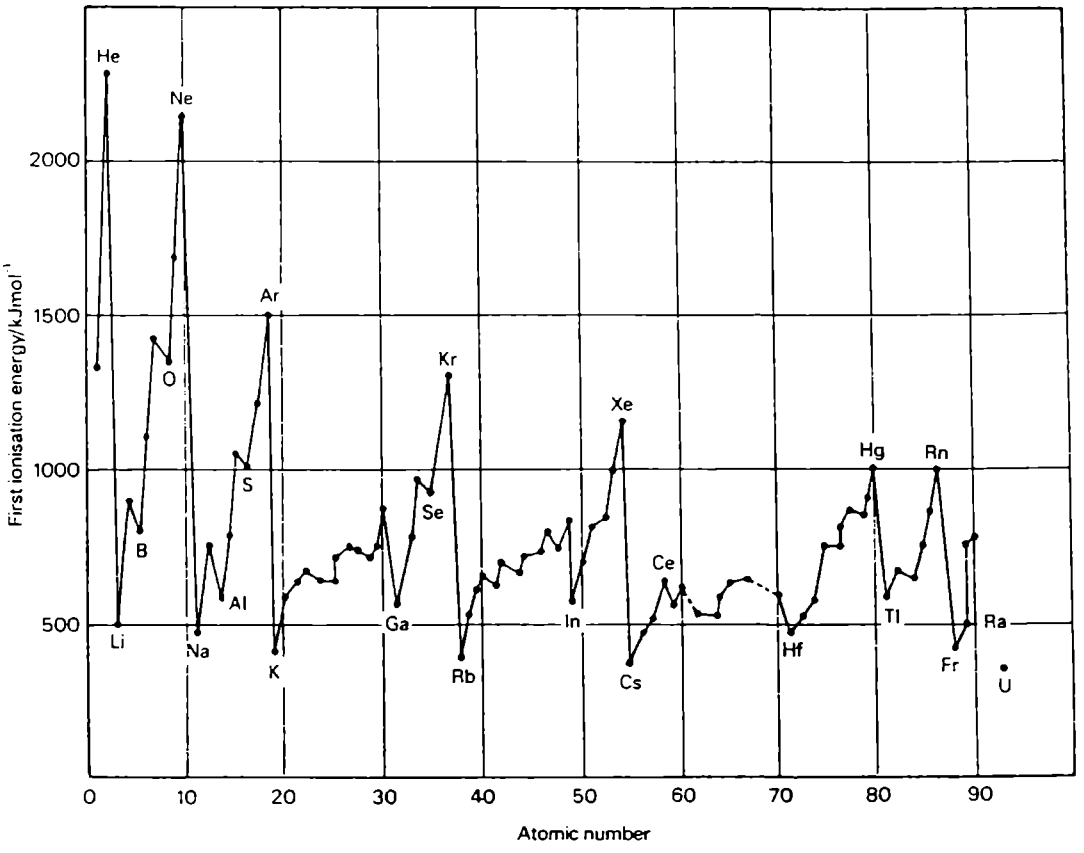

Fig. 2.2 The first ionisation energies of the elements

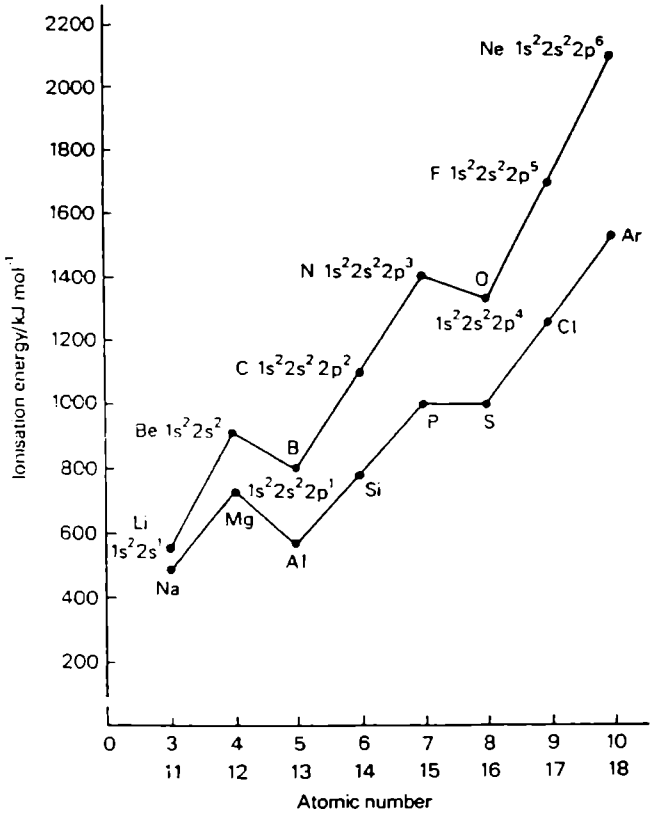

Fig. 2.3 The variation of first ionisation energies for the second and third Periods

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Fig. 6.4 shows the successive ionisation energies for magnesium. Because the energy required to remove the eleventh electron from a magnesium atom is over one hundred times the energy required to remove just one electron, it is convenient to use a logarithmic plot on the y-axis.

The electronic structure of magnesium is $1s^2 2s^2 2p^6 3s^2$. The energy required to remove the first two electrons is relatively low. This corresponds to the loss of the two 3s electrons. To remove a third electron needs much greater energy because this electron is close to the nucleus in a 2p orbital. There is a steady increase in energy required as electrons are removed from 2p and than 2s orbitals. The removal of the eleventh and twelfth electrons requires much greater amounts of energy, as these electrons are closer to the nucleus in the 1s orbital.

The distinction between **ionisation energy** and **electrode potential** should be clearly understood. **Ionisation energy** is the energy required to remove an electron in the gas phase.

$$M(g) \rightarrow M^+(g) + e^-$$

The **electrode potential** applies to the loss of an electron not in the gas phase.

$$M(s) \rightarrow M^+(aq) + e^-$$

The **electrochemical series** is a list of metals in order of the electrode potential. The order of ionisation energies is not necessarily the same.

2.5. Electron Affinity

Electron affinity is the energy change when one mole of isolated gaseous atoms gains one mole of electrons to form a mole of negatively charged ions.

$$X(g) + e^- \rightarrow X^-(g)$$

It is the atoms of elements on the right hand side of a Period which readily accept electrons to form negative ions. In these atoms there are greater nuclear charges to attract electrons. The electron affinities of chlorine, bromine and iodine are -364, -342 and -295 kj mol^{-1} respectively. In each case the value is negative as energy is released.

2.6. Electronegativity

The tendency of an atom to attract an electron to itself is called **electronegativity**. The electronegativity of an element can be regarded as related to ionisation energy and electron affinity, and can be evaluated in various ways. In a covalent bond such as

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between two chlorine atoms, the two atoms attract the pair of electrons in the bond equally. However in hydrogen fluoride, because fluorine is more electronegative than hydrogen, the pair of electrons is attracted more by the fluorine than the hydrogen. This results in a slight separation of charge.

$\delta^+ \delta^-$

H-F

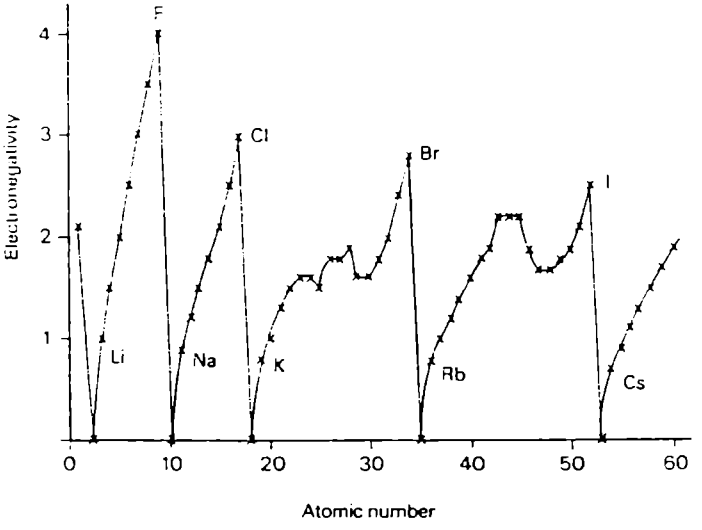

Fig.6.5 Variation of electronegativity with atomic number

Fig. 6.5 shows the variation of electronegativity (according to the values obtained by Pauling) with atomic number for the first 60 elements.

In any group of the Periodic Table there is a decrease in electronegativity down the Group. Across a Period there is an increase in electronegativity from the left to right. Elements in the top right hand corner of the Periodic Table are therefor most electronegative.

In bond formation, the difference in electronegativity between two atoms will determine whether the bonding is predominately ionic or covalent.

2.7 Atomic and ionic radii

The atomic radius can be determined by X-ray or electron diffraction. In any period there is a **decrease** in atomic radius from left to right. This surprises many students, because from sodium to chlorine there is an addition of 6 protons, 6 electrons and a number of neutrons and in spite of this atomic radii fall from 0.157nm to 0.099 nm. The explanation is that the extra electrons are being added to the same 3s and 3p orbitals (therefore there is no increase in size) but the extra nuclear charge attracts these electrons drawing them closer to the nucleus.

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For the elements in a Group of the Periodic Table, the atomic radii increase down in the Group. Down the Group, extra electrons are added to additional orbitals. Despite the extra nuclear charge and, because of increased screening, there is a net increase in atomic radius down the Group.

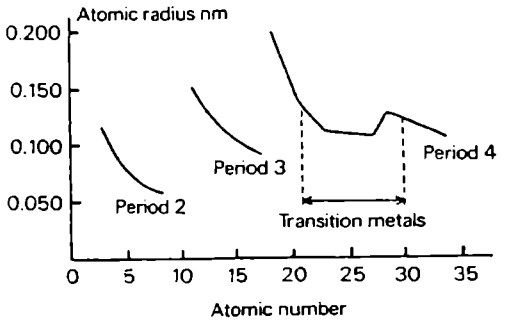

Fig. 6.6 Graph of atomic radius against atomic number

Fig. 6.6 shows a graph of atomic radius against atomic number. The trends in ionic radii down a Group are similar to those for atomic radii.

Cations (*i.e.* positive ions) have a smaller radius than the corresponding atoms.

E.g. Na 0.157nm Na^+ 0.098nm

The removal of one electron from a sodium atom empties the 3s orbital. The outer electrons is therefore in a 2p orbital.

Anions have a larger radius than the corresponding atom because of repulsion between the electrons. There is no extra nuclear charge.

E.g. F 0.064nm F^- 0.133nm

The three ions Na^+, Mg^{2+} and Al^{3+} are isoelectronic, i.e. they contain the same number of electrons in an arrangement $1s^2 2s^2 2p^6$. The ionic radii of these ions are 0.098, 0.065 and 0.045nm respectively. The decreasing radius is due to the additional nuclear charge-Na^+ contains 11 protons, Mg^{2+} 12 and Al^{3+} 13.

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2.8. Other properties

Oxidation states vary regularly through the Periodic Table.

Atomic volume is another property which varies periodically through the Periodic Table. Historically, Lothar Meyer plotted this graph to show periodicity within the Periodic Table before Mendeléef's table was devised. Atomic volume is the volume (in cm^3) of one mole of the solid element. A graph of atomic volume against atomic number is shown in Fig. 2.7.

Similar curves are obtained if other properties such as melting point, boiling point, enthalpy of fusion are plotted against atomic number.

2.9. Diagonal relationships

We will see obvious relationships between elements in the same Group of the Periodic Table. There are also trends within a Period.

In addition to these, there are similarities between elements diagonally related in the Periodic Table. The best example of this is probably the relationship between lithium and magnesium. The diagonal relationship is, however, limited to elements in the top left hand corner of the Periodic Table.

Lithium and magnesium have similar electronegativities and the atomic and ionic radii are similar. As a result of these similarities, there are considerable similarities in the chemistry of these two elements. For example:

(i) Lithium and magnesium form nitrides when burnt in nitrogen. These solid nitrides react with water to form ammonia.

$$6Li(s)+N_2(g) \rightarrow 2Li_3N(s)$$

$$3Mg(s)+N_2(g) \rightarrow Mg_3N_2(s)$$

$$Li_3N(s)+3H_2O(l) \rightarrow 3LiOH(aq)+NH_3(g)$$

$$Mg_3N_2(s)+6H_2O(l) \rightarrow 3Mg(OH)_2(s)+2NH_3(g)$$

(ii) Many of the salts of lithium and magnesium are insoluble in water. In this lithium differs from other alkali metals. Lithium chloride and magnesium chloride are soluble in organic solvents showing a tendency to covalent bonding.

Other common examples of diagonal relationship are given by beryllium and aluminium and boron and silicon.

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2.10. Group 0 elements

The noble gas elements were discovered after the Periodic Table had been devised. Their lack of reactivity was the reason for the delay in their discovery. The gases are helium He, neon Ne, argon Ar, krypton Kr, xenon Xe and radon Rn, and all are present in air.

The gases are all monatomic and sparingly soluble in water. The melting and boiling points increase regularly with increasing atomic number.

Compounds of noble gases are difficult to produce. The best known compound is xenon tetrafluoride which is prepared by heating xenon and fluorine together at 400°C under a pressure of 13 atmospheres.

$$Xe(g)+2F_2(g) \rightarrow XeF_4(s)$$

Xenon tetrafluoride is a colourless crystalline solid. It is hydrolysed by water to produce xenon(VI) oxide.

$$6XeF_4(s)+12H_2O(l) \rightarrow 4Xe(g)+3O_2(g)+24HF(g)+2XeO_3(s)$$

The structure of xenon tetrafluoride is shown in Fig. 2.8.

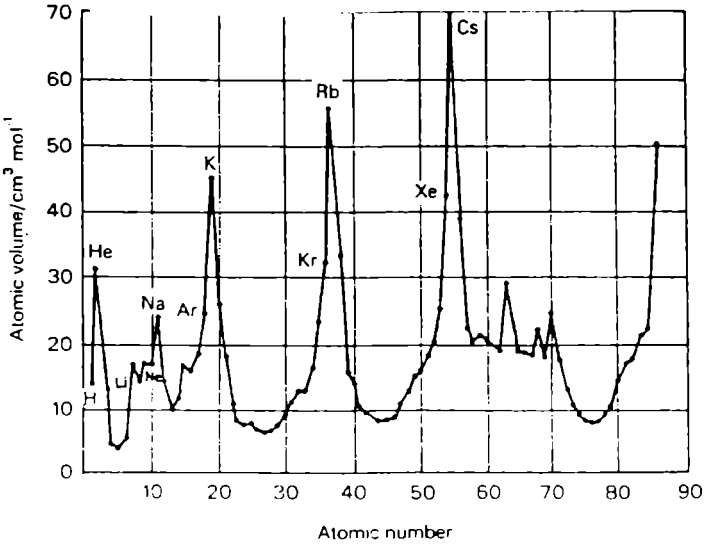

Fig.2.7 Graph of atomic volume against atomic number

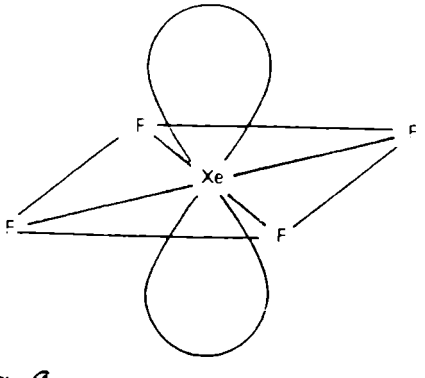

Fig.2.8 Structure of xenon tetrafluoride

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III.3The States Derived from Electronic Configurations

In general, a given electronic configuration does not correspond to a single *state* of the atom or ion. For our purposes, we shall regard a state as being characterized by particular values of (1) energy, (2) orbital angular momentum and (3) spin angular momentum. A state so characterized corresponds to the spectroscopist's *multiplet*. The term multiplet is used because, in fact, there are a number of components of the state which, in general, differ in energy by much less than one such state differs from another. These components of the state or multiplet have different values of the total angular momentum, which is a result of the combination of the orbital and spin angular momenta. Now the three characteristic quantities of a state of the system have magnitudes which are determined by the manner in which the three corresponding quntities foe ech of the individual electrons combine to produce the resultant quantities for the entire group of electrons. Even for the simplest cases, this is a complicated matter which cannot be dealt with entirely rigorouseli. However, we are fortunate in finding, from experiment, that for the lighter atoms (up to, approximately, the lanthanides) nature follows a scheme which can be understood to a fairly accurate level of approximation using a set of relatively simple rules. This set of rules may be designated the *Russell-Saunders* or *LS* coupling scgheme, and it forms the subiect of this section.

Each electron in an atom has a set of quantum numbars, n, l, m_l, m_s; *it* is the last three which are of concern here. Just as l is used, as $\sqrt{l(l+1)}$, to indicate the orbital angular momentum of a single electron, there is a quantum number L such that $\sqrt{L(L+1)}$ gives the total orbital angular momentum of the atom. The symbol M_L is used to represent a component of L in a reference direction and is analogous to m_l for a single electron. Similarly, we use a quantum numbar S to represent the total electron spin angular momentum, given by $\sqrt{S(S+1)}$, in analogy to the quantum number s for a single electron. There is the difference here that s is limited to the value 1/2, whereas S may take any integral or half-integral value beginning with 0. Components of S in a reference direction are designated by M_S, analogous to m_s.

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Symbols for the states of atoms are analogous to the symbols for the orbitals of single electrons. Thus the capital letters, *S, P, D, F, G, H,* ... are used to designate states with L = 0, 1, 2, 3, 4, 5, ... The use of S for both a state and a quantum number is unfortunate, but is practice seldom causes any difficulty.

The complete symbol for a state also indicates the total spin, but not directly in terms of the value of S. Rather the number of different M_S values, which is called the *spin multiplicity,* is used. Thus, for a state with S = 1, the spin multiplicity is 3 because there are three M_S values, 1, 0, - 1. In general the spin multiplicity is equal to $2S + 1$, and is indicated as a left superscript to the symbol for L. The following examples should make the usage clear.

For $M_L = 4$, $S = \frac{1}{2}$, the symbol is ^{2}G

For $M_L = 2$, $S = \frac{3}{2}$, the symbol is ^{4}D

For $M_L = 0$, $S = 1$, the symbol is ^{3}S

In speaking or writing of states with spin multiplicities of 1, 2, 3, 4, 5, 6, ... we call them respectively, ***singlets, doublets, triplets, quartets, quintets, sextets,*** ... Thus, the three states shown above would be called doublet G, quartet D and triplet S, respectively.

As in the case of a single electron, we may sometimes be interested in the total angular momentum, that is the vector sum of L and S. For the entire atom this is designated J. When required, J values are appended to the symbol as right subscripts.

For example, a ^4D state may have any of the following J values, the appropriate symbols being indicated:

L	M_S	J	*Symbol*
2	$\frac{3}{2}$	$\frac{7}{2}$	$^4D_{7/2}$
2	$\frac{1}{2}$	$\frac{5}{2}$	$^4D_{5/2}$
2	$-\frac{1}{2}$	$\frac{3}{2}$	$^4D_{3/2}$
2	$-\frac{3}{2}$	$\frac{1}{2}$	$^4D_{1/2}$

In order to determine what states may actually occur for a given atom or ion, we begin with the following definitions, which represent the essence of the approximation we are using:

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$$M_L = m_l^{(1)} + m_l^{(2)} + m_l^{(3)} + \ldots + m_l^{(n)}$$

$$M_S = m_s^{(1)} + m_s^{(2)} + m_s^{(3)} + \quad + m_s^{(n)}$$

in which $m_l^{(i)}$ and $m_s^{(i)}$ stand for the m_l and m_s values of the *i*th electron in an atom having a total of *n* electrons.

In general it is not necessary to pay specific attention to all the electrons in an atom when calculating M_L and M_S since those groups of electrons which completely fill any one set of orbitals (*s, p, d,* etc.) collectively contribute zero to M_L and to M_S. For instance, a complete set of *p* electrons includes two with $m_l = 0$, two with $m_l = 1$ and two with $m_l = -1$, the sum, 0 + 0 + 1 + 1 - 1 - 1, being zero. At the same time, half of the electrons have $m_s = 1/2$ and the other half have $m_s = -1/2$, making M_S equal to zero.

The generalization to any filled shell should be obivous. Therefore, we need only concern ourselves with partly filled shells.

III.4Current Concepts of Valence. Oxidation Numbers.

Redox Reactions

Valence is one of the basic concepts in chemistry, including inorganic chemistry, and has played an invaluable part in its development. Knowing the valences of the reacting atoms and the stoichiometry of chemical reactions dependent on them makes it possible to control the reactions and to perform all the necessary calculation involved in chemical engineering. Intimate knowledge of inorganic chemistry and, more specifically. the valences of chemical elements was instrumental for Mendeleyev when formulating the periodic law. As a matter of fact, valence was the main criterion for Mendeleyev who used it when questions arose as to where precisely in the periodic table to place elements (e.g., cobalt and nickel) in increasing order of atomic weight.

Today, the valence "in terms of hydrogen" or "in terms of oxygen" in Mendeleyev's sense is taken into account in various versions of the periodic system and used in evaluating the composition and properties of the compounds formed by the elements belonging to a particular group of the periodic table.

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In short, the concept of valence has played a role in the evaluation of chemistry, whose importance cannot be overestimated. Yet it should be pointed out that the rapid development of the theory of chemical structure has brought to light new facts that are pertinent to the properties of chemical elements but do not fit the older definition of valence.

In various textbooks the following definition of valence can be found:"Valence is a number of univalent atoms with which an atom of the given elements can combine (or which it can substitute) in forming a molecule". Valence is also defined as "the property of atoms of an element to combine with a definite number of atoms of other elements". Finally, valence is"a number of chemical bonds to other atoms which an atom forms upon chemical combination".

Such definitions, however, fail to grasp the entire diversity of the phenomena associated with valences of the reacting atoms. Moreover, these and other similar definitions have different implications: the first definition has to do with compounds of molecular structure, the second interprets valence not as a number but a rather vague ratio (since it implies interaction between any atoms and not univalent ones), and the third definition involves the number of bonds rather than atoms, without saying a word as to the nature of these bonds.

At present, the theory of valence is usually understood as the theory of bonding, while valence implies the totality of interactions between atoms co-existing within a substance. These interactions differ in nature and in the energies involved in the chemical combination. They also include the electrostatic forces between charged particles as well as covalent interactions resulting from the formation of new electron pairs and from the redistribution of already existing pairs among the reacting atoms or groups of atoms (donor-acceptor, p-dative, and other bonds).

While evaluating the valences in real chemical compounds, one must consider the formation of localized and delocalized, directed and nondirected, saturated and unsaturated bonds. Significantly, it never happens in reality that only one type (in physical terms) of interaction occurs, say, only an ionic or only a covalent one.

Even in such a compuond as cesium chloride which is made up of ions represented by atoms of elements widely different in electronegativity, the effective charge on the cesium atom, determined experimentally and calculated using semiempirical quantum-chemical methods, does not exceed +0.8. This is indicative of the major contribution of the covalent forces to formation of cesium chloride.

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The determination of the number of bonds as well as atoms adjacent to the given atom in a particular chemical compound (coordination number) is especially difficult if the substance is not a molecular compound (the first of the above definitions of valence) but a solid usually crystalline one consisting of alternating infinite chains, atomic layers or three-dimensional groups of atoms carrying a positive or negative charge. For instance, in ordinary sodium chloride which is believed to consist of univalent ions of sodium and chlorine, the number of bonds formed by the two elements is not equal to unity at all. In fact, every ion of sodium and chlorine in crystalline sodium chloride is surrounded by six oppositely charged ions.

Therefore, even if it is assumed, for simplicity, that the interaction involves only atoms in direct contact with one another and the interaction which is extremely important in the second, third, and subsequent "coordination spheres" is ignored, the number of bonds will be other than unity. Since the coordination number of sodium and chlorine in crystalline sodium chloride is six and all of the six bonds are equivalent, then it is logical to assume that sodium and chlorine combine with six atoms of the partner element and, consequently, the valence of sodium as well as chlorine is six.

When we say that sodium and chlorine in sodium chloride are univalent, we disregard the true structure of the compound, proceeding instead from its stoichiometric formula (NaCl) which is only representative of the composition of the compound (the molar ratio of the reactants). Often, however, especially in school and other simplified chemistry courses, such an approach leaves the wrong impression that all substances, including sodium chloride, consist of molecules[3].

The estimation of the number of bonds in compounds of the molecular type is not always easy either. For instance, if there is no problem in determining the valence of carbon in methane, establishing the number and multiplicity of bonds in diatomic molecules of oxygen, nitrogen, and chlorine is a difficult task.

It is particularly difficult to assign a number to the valence of partner atoms in molecular compounds such as nickel tetracarbonyl, iron pentacarbonyl, and others, as well as in compounds similar to dibezenechromium.

Thus, the real valences cannot be merely expressed in terms of a number; what is necessary is a complete description of the crystal or molecular structure, investigation of the electron density distribution, evaluation of the contribution of electrostatic and covalent forces, establishing the

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presence or absence of multiple and delocalized bonds, and finding bridging atoms or groups of such atoms as well as multiple-site interactions.

Finally, in studying crystalline compounds of the ionic type account should be taken of possible formation of nonstoichiometric compounds. A case in point is ferrous oxide whose stoichiometric composition with an iron-to-oxygen ratio of 1:1 is beyond the region of homogeneity, or titanium monoxide characterized by an extremely broad homogeneity region ($TiO_{1.25}$- $TiO_{0.6}$).

To study valences, chemical research workers have been developing experimental techniques and calculation methods which yield data necessary for adequate description of real compounds.

The structural complexity of all compounds, even those that seem to be simple (in stoichiometric terms), has made it necessary to introduce conventional simplified concepts, including that of the "oxydation number". This concept has practically superceded that of valence (as a number) in modern chemistry textbooks. When we say "valence". we actually mean "oxidation number".

How are valence and oxidation number related to each other? Should we retain the old concept of valence in the sense used by Mendeleyev when be worked on his periodic system? Does not the viability of the old concept of valence prove that we still take it into account when we assign coefficients to the atoms involved in redox and exchange reactions and that the classification of the types of compounds formed by a particular element is based on valence?

Before we answer these questions, let us make sure we understand what "oxidation number" means. This concept can be traced back to Berzelius. His theory of "electrovalence", which was later rejected, was based on the assumption that all chemical compounds have only ionic bonds. Electrovalence could be positive or negative. The same assumptions underlie the oxidation number concept[4]. The oxidation number is often defined as the "electric charge of an atom in a compound, calculated assuming that the compound consists of ions"[4]

In this case, the oxidation number (state) is to be designated by an Arabic numeral proceded by a "+" or "–" sign. The oxidation number of an element, when it "is not written in the formula of a compound", can also be "designated by a Roman numeral in brackets after the symbol of the element" (ibid.).

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As can be inferred from the above definition, the oxidation number revives the basic postulates of the electrovalence theory and, consequently, represents a legitimized formal approach to the structure of chemical compounds.

It is assumed that all bonds in a chemical compound are purely ionic, although this is not so even in the case the most ionically structured chlorides of alkali metals, formed by partner elements with widely different electronegativity. Besides, the stoichiometric formula which is essentially representative of only the molar ratio of atoms in the compound is taken as a structural unit making up the compound in question. For example, in order to determine the oxidation number of atoms of the constituentelements of sodium chloride, the stoichiometric formula NaCl should be regarded as a structural unit. then, assuming that the oxidation number of alkali metal ions, just as protons, is always +1 and, proceeding from the law of electroneutrality of chemical compounds, it may be assumed that the oxidation number of chlorine in sodium chloride is -1.

In the case of halides of alkali metals, the discrepancy between the magnitude of the effective charge, formally calculated according to the rules of definition of the oxidation number, and that of the true charge on the atoms of a crystalline compound is minimal. However, in more complex (from the stoichiometric and structural standpoint) compounds, this discrepancy is often so wide that the oxidation number becomes for them a purely arbitrary quantity. For instance, assuming that the oxygen atoms in chemical compounds always have oxidation number -2, that of the chromium atom is chromates turns out to be equal +6, while that of the chlorine atom in perchloric acid and perchlorates is +7, and so on.

At the same time, as has been firmly established, the chromium-oxygen or chlorine-oxygen bonds in the above-mentioned compounds, just as in other similar oxo-anions, are predominantly covalent and of a complex nature, including localized σ-and delocalized π-bonding. The effective positive charge on the atom of the element constituting an oxo-anion never exeeds 2+ in such compounds.

Chromium and chlorine ions with charges 6+ and 7+ can be obtained experimentally, but by physical methods involving atomic excitation rather than by "chemical" means. It is absolutely clear, however, that the high-charge cations detectable by spectral or other physical techniques in high-energy fields cannot survive for a more or less long period of time once they find themselves in an ordinary chemical medium. Their extremely high effective charge polarizes the electron shells

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of the adjacent atoms so strongly that the electron density undergoes rapid redistribution and the electron shell disrupted in the physical experiment is "restored".

Hence, the concept of "oxidation number", just as that of "electrovalence" rejected earlier, is applicable only for formal classification of chemical compounds and reactions.

Yet, this notwithstanding, the oxidation number is often thought of as a real quantity: the state of oxidation is identified with the magnitude of the charge on respective atoms or at least regarded as proportional to the charge. Such an approach to the oxidation number is based, in particular, on its being used in electronic and ion-electron equations of redox reactions.

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IV. The chemical bond

The chemical compounds contain joint atoms through chemical bond. Through chemical bond the atoms stabilized as cations or anions with a noble gas configuration (e.g. O^{2-}, Cl^{-}, N^{3-}, K^{+}, Mg^{2+}, Al^{3+}) or pseudo noble gas (e.g. Zn^{2+}, Cd^{2+}, Ga^{3+}).

The metals lose the outer shell electrons to form stable cations and the nonmetals require electrons to form anions. These processes are called ionic valence states and may be predicted from the electronic configurations. Another mode to stabilize the atoms in a chemical compound is to form covalent bond between the atoms. The unpaired electrons of the outer shell are shared and form a covalent bond. In this way each of atoms obey the octet rule.

IV.1. THEORETICAL TREATMENT OF IONIC BOND

The Nature of the Ionic Substances

Most ionic compounds are formed by combination of elements near "opposite ends" of the periodic table. They are usually oxides, sulphides or halides of the electropositive metals such as those of groups I, II, III and the transition series. The main requirement for the formation of the ionic compounds, that is, those solids which consists of an array of positive and negative ions held together almost entirely by the coulomb forces between the oppositely charged ions, are the metal ions which have a relatively low ionization potential and that the nonmetals atoms or radicals have a relatively high electron affinity.

IV.1.1. Lattice Energies of Ionic Crystals

As an example of an idealized ionic substance let us consider a 1:1 compound of the type $(M^{+})(X^{-})$. M^{+} is the cation, spherical in shape, incompressible and X^{-} is the spherical anion, also incompressible and having a definite size. This kind of model is commonly called a hard sphere electrostatic model. When these cations and anions are brought together in large and equal numbers, they will arrange themselves in a regular array in which they trend to occupy the minimum volume and have the least electrostatic energy. This arrangement adopted is that is shown in the Figure IV.1.and this type of lattice arrangement occuring in sodium chloride.

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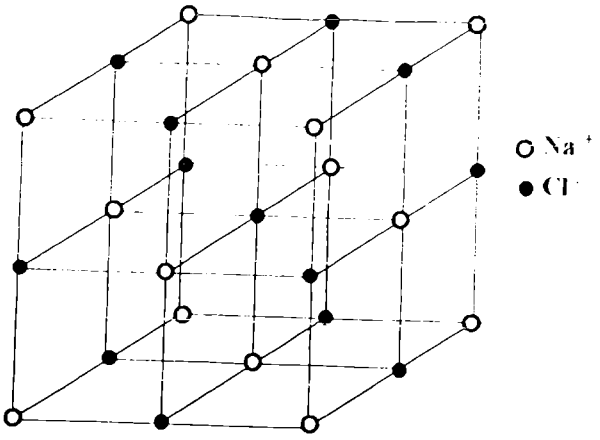
Figure . .1.The sodium chloride structure



M-X is the distance r; Using the figure IV.1 and the simple trigonometry it can be shown that M^+ ion is surrounded by six X^- ions (nearest neighbors) at a distance r, twelve ions (second nearest neighbors) at a distance $\sqrt{2}$ r, eight more distant X^- ions at $\sqrt{3}$ r, six M^+ ions at 2r, twenty-four more ions at $\sqrt{5}$ r, etc .

The electrostatic interaction energy of the M^+ ion with each of these surrounding ions is equal to the product of the charge on each ion, Z_e^+ and Z_e^- ,divided by the distance. Hence the electrostatic energy can be written:

-six attraction at the distance r

-twelve repulsions at the distance$\sqrt{2}$ r

-eight attractions at the distance $\sqrt{3}$(corners)

- six attractions at the distance 2r

$$U= \frac{6e^2 (Z^+)(Z^-)}{k\,r} + \frac{12e^2(Z^+)^2}{k\sqrt{2}r} + \frac{8e^2}{k\sqrt{3}r}(Z^+)(Z^-) + \frac{6e^2}{k2r}(Z^+)^2 + \ldots$$

$$U_{NaCl}= \frac{-ke^2 |z|^2}{r}\left(\frac{-6}{\sqrt{1}} + \frac{-12}{\sqrt{2}} + \frac{+8}{\sqrt{3}} + \frac{-6}{\sqrt{2}} + \frac{+24}{\sqrt{5}}\right)$$

The sum is called the Madelung's constant ,and it is characteristic and it is characteristic of the geometrical of the go arrangement and independent of the ions of their charges.

If we made (N ion pairs) of the compound MX, then NE would be the energy of the process.

$$M^+_{(g)} + X^-_{(g)} = MX_{(s)}$$

Thus NE is the electrostatic potential energy per mole for a hard-sphere ionic with NaCl structure.

We know that real atoms are not rigid spheres, and their equilibrium separation in are ionic must therefor be a consequence of some short-range repulsive force due to

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overlapping of their electron clouds which comes into play as they approach. Born proposed the simple assumption that the repulsive force between two ions could be represented by the expression B'/r^n in which B' and n are constant characteristic of their of the ion pair concerned.

The repulsive energy of a particular ion in a crystal:

$$E_{rep} = B/ r^n$$

where B is related to B' by the crystal geometry. The total electrostatic energy of the crystal, that is, the inherent negative lattice energy, U, is then given by :

$$U = N (Z^+)(Z^-)e^2A/r + B/r^n$$

A is the Madelung constant.

There is a relation between B and n which may be determined if we recognize that in the equilibrium state of the crystal($r = r_o$) the energy is a minimum as a function of r. Thus :

$$\frac{dU}{dr} = O = - \frac{A (Z^+)(Z^-)Ne^2}{r_o^2} \frac{-nB}{r_o^{n+1}}$$

which yields:

$$B = \frac{A (Z^+)(Z^-)e^2}{n} \frac{r_o^{n-1}}{1}$$

and:

$$U = N (Z^+) (Z^-) A \frac{e^2}{r_o} (1-1/n)$$

To the lattice energy there are many contributions indicated in the tableIV.1

Table IV.1 components of Lattice energy

Energy	LiF	NaCl	CsI
Coulomb	-12.4	-8.92	-6.4
Repulsion	+1.9	+1.03	+0.63
Van der Waals	-0.17	-0.13	-0.48
Zero point	+0.17	+0.08	

The calculation of lattice energy of ionic compounds is very important since, in general, there are no direct way to measure them experimentally although they can be obtained from certain experimental data using the Born- Haber cycle.

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IV.1.2. The Born -Haber cycle

The heats of formation of various ionic compounds show tremendous variations. In general, we know that many factors contribute to the over-all heat of formation namely, the ionization potentials, electronic affinity, heats of vaporization and dissociation of the elements, and the lattice energy of the compound .The Born-Haber cycle is a thermodynamic cycle which shows the interrelation of these quantities and enables us to see how variations in heats of formation can be attributed to the variations in these individual quantities.

In order to construct the Born-haber cycle we consider the following thermochemical equations, using NaCl as an example:

$$Na_{(s)} = Na_{(g)} + \Delta H_{subl}(Na)$$

$$Na_{(g)} = Na^{+}_{(g)} + e^{-} + I_{Na}$$

$$1/2\ Cl_{2\,(g)} = Cl_{(g)} + 1/2\ \Delta H_{diss}(Cl_2)$$

$$Cl_{(g)} - e^{-} = Cl^{-}_{(g)} - A_{Cl}$$

$$Na^{+}_{(g)} + Cl^{-}_{(g)} = NaCl_{(s)} - U$$

$$Na_{(s)} + 1/2\ Cl_{2(g)} = NaCl_{(s)} \quad \Delta Hf \quad (NaCl)$$

Normally, ΔH_f, ΔH_{subl}, I and ΔH_{diss} are known. Direct measurement of electron affinities is usually rather difficult, and only for the halogens have really accurate values been obtained. Thus, the cycle is more commonly used for determine electron affinities. For example, the electron affinity of oxygen is a very important quantity which cannot be measured directly, if no other reason than that it is highly negative, namely -7.3 eV. This value has been obtained by applying the Born-Haber cycle to various ionic oxides.

IV.1.3. Ionic Radii

It is already apparent from the nature of the wave functions for atoms and ions that they have no definite size. The only way we can assign a radius to an atom or ion is to measure in one way or another how two atoms or ions can approach one another under the influence of forces of the magnitude encountered in chemical processes. For the ions in a crystal we can do this by considering the distance between the centers of two adjacent ions to be the sum of their ionic radii. From X-ray measurements of the ionic distances in a large number of ionic radii can be complited.

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One simple method for estimating the radius is based on the proposal that for a pair of isoelectronic ions, say Na^+ and F^- ,the radii will be inversely proportional to the effective nuclear charge to which the outer electrons are subject .According to the Slater's procedure, one obtaines for the shielding of outer (2s,2p) electron in the neon configuration the value 4.15 .For Na^+ (Z=11) and Z* =11- 4.15 = 6.85 which F^- (Z=9)and Z* = 9-4015=4.85.Thus ,the ratio of the radii r F^-/r Na^+ =4.85/6.85 =0.71

If now the sum of these radii is taken as the Na-F distance in NaF (2.31A°), the individual radii must be r F^-=1.35A°;r Na^+ = 0.96A°

IV.1.4. Some Important Types of Ionic Lattices

A great ionic compounds of the type M^+X^- occur with one of three structures; the sodium chloride (see the FigureIV.1),the cesium chloride (figure IV.3) or zinc ZnS (Figure IV.3) structure.

In an ionic lattice each ion is surrounded by a certain number of ions of the opposite sign; this number is called the coordination number of the ion. In three structures mentioned the cations have the coordination numbers 6,8 and 4,respectively.

The factors which contribute to the energy are the force between oppositely charged ions, which will increase with increasing coordination number, and the forces of repulsion, which will increase very rapidly if the ions of the same charge are squeezed together.

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IV.1.5. Other Electrostatic Interactions

a) Deformability and Polarizability of Elementary ions

Rule 1. Anions are more prone to deformation than cations. Anions have excess electrons which, when repulsing one another, loosen the electron shell of the ion. A loose electron shell is more susceptible to deformation than the more compact electron shell of a cation (under comparable conditions).

Rule 2. Among cations, ions with an 18-electron shell are the most susceptible to deformation (i.e., ions whose outer electrons occupy the *s, p,* and *d* levels). The deformability becomes less pronounced toward ions with an incomplete 18-electron shell or an 8-electron one. this is due to the 18-electron shell being looser. It may change its spatial extent in a much more appreciable manner than the electron shell of an inert gas.

Rule 3. In the case of ions of identical electrons shell configuration, their deformability diminishes with a decreasing negative charge and an increasing positive charge of the ion. For exemple, the deformability of ions of elements I and II of the shorter periods, which are neighbours in terms of their atomic numbers, varies as follows:

$$O^{2-} > F^{-} > Ne^{0} > Na^{+} > Mg^{2+} > Al^{3+}$$

$$\longrightarrow$$

Decreasing deformability

Such a pattern stems from the fact that, at a high positive charge of the ion, the electrons in the outer shells are more vigorously pulled toward the atomic nucleus, and the shells become more compact and less prone to deformation than at a low positive and especially negative charge.

Rule 4. The deformability of analogous ions increases with the ionic radius. For example, the deformability increases in the following series: $F^{-} < Cl^{-} < Br^{-} < I^{-}$ or $Li^{+} < Na^{+} < K^{+} < Rh^{+} < Cs^{+}$. The most susceptible to deformation among the cations of some alkali metals is the electron shell of the cesium ion, while among halogen anoins, it is the electron shell of the large iodine ion. Of course, the electron shell configuration plays a certain role here, too. For example, the single-charged cations with an 18-electron shell (Cu^{+}, Ag^{+}) undergo stronger

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deformations than the cations of the same charge and radius having an 8-electron shell, such as Be^{2+}, Al^{3+}, and Si^{4+}.

***b)* Deforming (or Polarizing) Effect of Elementary Ions**

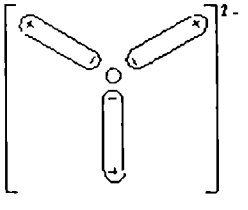
Rule 1. The deforming effect is usually exerted by cations, while in the case of anions, such as O^{2-} or F^-, it is less common.

Rule 2. The deforming effect increases with the cationic charge. For example, the polarizing effect increases in the series $Na^+ < Ca^{2+} < Y^{3+}$ — that is, from the single-charged sodium ion to the triple-charged cation of yttrium. Notably, the radii of these ions are virtually the same (1.06 C for Y^{3+} and Ca^{2+}, 0.98 C for Na^+). Their electronic structure is also the same, featuring an inert gas-type inner electron shell. Thus, it is the ionic charge that determines the amount of deformation in this series.

Rule 3. The deforming effect increases inversely with the cationic radius. For example, in the series $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, the deforming effect of the cesium ion is the least pronounced, while the deformation it undergoes is the strongest.

Rule 4. The deforming effect of a cation increases from ions with an 8-electron shell toward those with an incomplete and, especially, complete 18-electron shell. The double-charged cations of calcium, manganese, and zinc provide the best examples. Their radii are close in length, and they have, respectively, 8-electron, incomplete 18-electron, and complete 18-electron shells. The least pronounced deforming effect is exerted by Ca^{2+}, and the most pronounced one, by Zn^{2+} ($Ca^{2+} < Mn^{2+} < Zn^{2+}$).

An important consequence of deformation of the electron shells of atoms, ions and molecules, occuring during their interaction, is the counter and additional polarization effects. Consider the effect of counter polarization involving carbonates of metals. An isolated carbonate ion --- that is, one that is not affected by any fields, for example those produced by the adjacent cations, may be schematically represented as follows:



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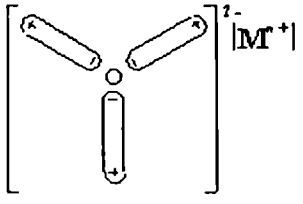
In this oversimplified scheme, the oxygen atoms are shown as dipoles whose negative pole is oriented toward the carbon atom. Such a representation is justifiable since the carbonate ion is essentially a covalent compound in which the maximum electron density is concentrated in the space between the carbon and oxygen atoms. Consequently, the electron density at the oxygen atoms in carbonate ions is shifted with respect to that of the neutral oxygen atoms or isolated O^{2-} ions toward the carbon. Let us now imagine that approaching as isolated carbonate ion is a positive charge of sufficiently high density, for example a positively charged M^{n+} cation. The oxygen atom which is statistically acted upon by the positive charge undergoes changes due to polarization, namely, the electron density shifts toward the positive charge sourse. As a result, the polarisation of this oxygen atom changes as compared with the polarization characteristic for the oxygen atoms in the carbonate ion, unaffected by the positive charge. The negative pole of the oxygen atom will now face the external cation, whereas facing the carbon atom will be the positive pole with minimum electron density:



Thus, pole reversal, or counter polarisation of the oxygen atom, takes place. As a result of the lowering of the electron density in the space between the carbon and counter-polarized oxygen, the covalent carbon-oxygen bond becomes weak. Therefore, a slight temperature effect on the counter-polarized carbonate ion is sufficient for such a bond to be partially destroyed.

Evidently, the higher the positive charge density (with all other conditions being equal) at the cation which causes counter-polarization of the carbonate ion, the lower the temperature at which the carbonate ion breaks down losing an oxygen atom: the reaction

$$M_2CO_2 \rightleftharpoons M_2O + CO_2$$

will proceed, for example for lithium carbonate, at a temperature of about 600 °C, while for sodium carbonate, it will proceed at a temperature above 800 °C. The carbonates of alkaline-earth

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metals are neighbors in the corresponding period of Mendeleev's table: alkaline-earth metals from smaller double-charged cations. In the general case, this pattern holds for salts formed by other oxo-anions as well, including nitrates, sulfates, perchlorates, and so on. It should be taken into account, however, that the relationship between the counter-polarizing effect and the thermal stability of chemical compounds may, sometimes, not be too simple if the dissociation proces is affected by several factors.

Here is an example. It would appear that the most thermally stable compound in the series of alkali metals is cesium carbonate because the single-charged cesium cation exerts the least pronounced polarizing effect among the cations of alkali metals due to its long radius. However, experimental evidence indicates that this compound is thermally even less stable than lithium carbonate. The reason for the reversal of thermal stability in the series of carbonates of alkali metals is the high volatility of the cesium oxides resulting from the dissociation of the carbonates. Volatilization of oxygen compounds of cesium and their egress from the reaction sphere shift the equilibrium of the thermal decomposition of the carbonate and, as a result, this process occurs at an abnormally low (from the standpoint of the polarization pattern) temperature. Thus, the polarization phenomenon or, more precisely, the counter polarization effect is not the only factor affecting the thermal decomposition of oxo-anions. Yet it is one of the major factors determining the course of the process. In cases where such side effects do not occur, an analysis of the polarization patterns gives better insight into the changes in particular chemical and physical properties of similarly structured compounds.

For a better understanding of the course taken by many important reactions, one must take into account the additional polarization effect. It resides in that a readily deformable anion may, in the own right, exert a polarizing action on a cation with a pronounced deforming capacity, provided it can be deformed. A case in point is cupric sulphide. The Cu^{2+} ion having an almost complete 18-electron shell acts upon the sulfur ion and deforms it. As a result, the latter becomes a dipole. Its electron shell is stretched toward the copper ion. Therefore, the negative charge oriented toward the Cu^{2+} ion increases. Since the copper ion also has a readily deformable electron shell, its constituent electrons are repulsed from the negative pole of the sulphur dipole. As a result, the Cu^{2+} ion also becomes a dipole, its positive pole being oriented toward the S^{2-} ion. This promotes the polarization of the sulphur ion, the S^{2-} dipole increases in size, which, in turn, leads to the further stretching of the electron shell of Cu^{2+} from S^{2-}, and so on.

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The tendency for additional polarization (or additional polarization effect) is particularly manifest in atoms (or ions on their basis) having a complete 18-electron shell. In analogous elements belonging to the same subgroup of the periodic system, the tendency for additional polarization increases within the subgroup from top downward, and the deformability of electron shells in the series increases as the atomic (ionic) radius increases.

Note that in subgroups of analogous elements having an 8-electron or incomplete 18-electron shell, the polarizing effect becomes more pronounced with an increasing atomic (or cationic) radius. Thus, we observe a tendency opposite to the one just described because the additional polarization effect is not typical of the atoms and ions lacking an 18-electron inner shell. It is this difference in the capacity to polarize and be polarized that is the main reason why the elements in the main and secondary subgroups of the periodic system display different tendencies for the formation of compounds with the highest and lowest oxidation states.

Consider, by way of example, the main and secondary subgroups of Groups IV, V, and VI of the periodic system.

The subgroups of titanium (Ti, Zr, Hf), vanadium (V, Nb, Ta), and chromium (Cr, Mo, W) are characterized by the stability of compounds with lower oxidation numbers decreasing from top downward. Indeed, it is quite easy (e.g., by reduction with zinc in hydrochloric acid) to obtain the derivatives of Ti(III), V(IV, III, II), and Cr(III, II), while their heavy analogues do not lend themselves to reduction under the same conditions. On the contrary, in the subgroups of germanium (Ge, Sn, Pb), arsenic (As, Sb, Bi), and sulphur (S, Se, Te), the stability of compounds with higher oxidation numbers decreases from top downward. For example, lead is much more stable in the oxidation state 2+ than 4+, whereas for its light analogue, germanium, the oposite is true. The same applies to the subgroups of arsenic and sulphur. For instance, the compounds of Bi(V) are less stable than the analogous compounds of arsenic.

This tendency is sometimes explained in terms of so-called "inert electron pair" present in atoms with an 18-electron shell. However, the polarization theory may be effective in explaining this tendency. Tndeed, the instability of, say, compounds of Pb(IV) or Bi(V) which are the heaviest and largest atoms in their respective subgroups can be explained by their tendency for additional polarization resulting in disturbance of the electron shells of the partner atoms due to mutual polarization. As a consequence, electrons are rearrenged between the cationic and anionic forms, which is interpreted as a restoration process. For example, in the reaction

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$$PbCl_4 \rightarrow PbCl_2 + Cl_2$$

lead(IV) restores its electron shell through incorporation of the electrons belonging predominantly to the chlorine atoms in the polar covalent compound $PbCl_4$.

Thus the different stability trends in compounds with the lowest and highest oxidation states in the main and secondary subgroups of the periodic system are adequately explained by an increases (with an increasing radius of the particle) in the deformation of atoms due to additional polarization in the subgroups of elements with an 18-electron shell, this effect being absent in the subgroups of elements with an 8-electron shell.

Now folow some other examples of polarization interactions affecting the properties and structure of inorganic compounds.

c) Effect of Polarization on the Physical and Chemical Properties of Substances

c1) Changes in the Structure and Bond Type in Compounds Identical in Composition, Depending on the Polarization Properties of the Chemically Linked Partners

Ionic bonding may, generally speaking, be regarded as a consequence of polarization interaction between neutral atoms, for example

$$Na^{\cdot} + Cl^{\cdot} \rightarrow Na^{+} + Cl^{-},$$

resulting in the rearrangement of electrons and the formation of oppositely charged ions. The polarization theory, however, usually proceeds from the opposite, it being assumed that oppositely charged ions, isolated at first, have already been formed. They come close together and polarize each other. Obviously, the polarization interaction must be different depending on the species of the converging ions. The greater the degree of overlap of the electron shells of the ions as a result of their mutual polarization, the greater the departure of the bond betweenthe particles from the purely ionic one and the more closely it approaches a covalent bond.

The changing polarization interaction between oppositely charged ions in periods and groups of the periodic system is often one of the main reasons for changes in the crystal structure type, melting point, state of aggregation, and coloration of the compounds. The contribution of covalent forces increases, in particular, in the following series of halides of elements belonging to period II:

$$LiCl \rightarrow BeCl_2 \rightarrow BCl_3 \rightarrow CCl_4.$$

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This is due to the ionic radii (calculated) decreasing in the series: $Li^{+} > Be^{2+} > B^{3+} > C^{4+}$ with a simultaneous increase in the ionic charge, which also contributes to the intensification of the polarization interaction E – Cl and initiates a transition from predominantly ionic compounds (of the LiCl or $BeCl_2$ type) to predominantely covalent ones (of the BCl_3 or CCl_4 type).

In period III, the cations of the elements of the corresponding groups are large in size, and their polarizing effect is less pronounced, as compared to the corresponding cation of period II. Therefore, the shift toward the covalent bond in halides of the elements belonging to period III is slower in the direction from left to right, as opposed to period II: the properties of $AlCl_3$ are similar to those of $BeCl_2$, while $SiCl_4$ is in this respect to BCl_3 . This is one of the manifestations of the so-called "diagonal rule".

The effect of polarization interactions on the bond type is vividly illustrated by changes in the melting points of halides of alkali metals. If the $M^{+} – F^{-}$ bond has been ionic in all instances, one would have expected the electrostatic interaction between the ions to be the strongest (and the melting point to be the highest) for LiF because the single-charged Li^{+} and F^{-} ions are the smallest in the series under consideration. On the contrary, the weakest electrostatic interaction (and the lowest melting point) might be observed in CsI because the Cs^{+} and I^{-} ions are the largest, hence the distance between the positive and negative centres in this compound must also be the longest.

The real pattern of changes in the melting points of fluorides, chlorides, bromides, and iodides of alkali metals is far from the rectilinearity expected assuming a purely ionic interaction in these compounds. As can be seen from Figure 1, the relations between the melting point and alkali metal cation radius are rectilinear only in the case of the heaviest alkali metals. At the same time, the halides of Li and Na exhibit abnormally low melting points. This anomaly is especially manifest in the case of iodides.

The above effect can be attributed to the polarization interaction which is particularly strong for the ion pair Li^{+} - I^{-}: the small "rigid" lithium ion strongly polarizes the large loose iodine ion. The polarization of the latter by the former results in that the ionic structure becomes deformed an starts resembling a molecular one. As consequence, the melting poiont goes down, as is typically the case with substances of molecular structure. Figure 1 indicates that maximum

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departure from ionic model is observed in iodides of alkali metals, that in fluorides being the least pronounced (as would be expected).

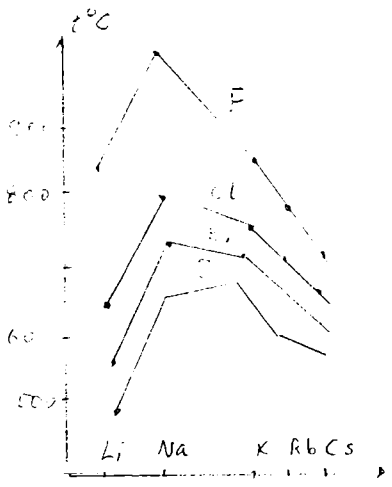

Fig. 1 Melting point of alkali-metal halides

Bromides and chlorides represente an intermediate situation. In the case of fluorides, only the lithium compound has an abnormally low melting point - that is, it tends toward molecular structure. Beginning with NaF in the series of fluorides, we observe a monotonic relationship between the melting point and alkali metal cation radius, which is close to rectilinear. This gives every reason to assume a minor contribution of the covalent forces to the formation of fluorides of alkali metals from Na through Cs or, in other words, an insignificand polarization interaction between the cation and anion in these compounds.

Interestingly, the melting points of salts having similar crystal structure and short interatomic distances may differ widely if the electron shells of the ions have different structures. Examples include NaCl and AgCl which have identical crystal structures and closely similar lattich parameters (d^{NaCl} = 2.81 C, d^{AgCl} = 2.74 C). Their melting points, though, differ widely: 800°C for NaCl and 457°C for AgCl, which is due to the pronounced polarization effect in AgCl (because of the 18-electron shell of the silver cation), causing a shift from ionic to molecular structure.

Strong polarization interaction often leads to the alteration of the crystal structure type. For example, the increasing polarizing effect of the cation or polarizability of the anion in binary compounds results in a gradual decrease in the coordination number of the cation and in a transition from the ionic structure (of the CaCl or Na Cl type) to a molecular one (of the ZnS type). A good illustration is the series AgCl → AgBr → AgI where the structure changes from that of the NaCl (AgCl, AgBr) type to that of the ZnS (AgI) type by virtue of the increasing polarizability of the anion from Cl^- to I^-, the deviation of the distances between the centres of

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the positives and negative charges from the sum of ionic radii increasing significantly (by 0.17 C for AgCl, by 0.21 C for AgBr, and by as much as 0.34 C for AgI). The centres of the positive and negative charges come closer together as a result of increasing polarization interaction between the ions from AgCl to AgI.

Interestingly, the type of structure is often determined not only by the ratio between the radii of the cation and anion. For example, in the case of MgO, this ratio equals 0.59, which leads to a structure of the NaCl type. In the case of ZnO, however, we are dealing with a ZnS rather than a NaCl-type structure, althuogh the ratio between the radii of Zn^{2+} and S^{2-} is, in this case, even greater than with MgO. The reason lies in the strong polarization interaction of the loose Zn^{2+} and O^{2-} ions, giving rise to a structure close to molecular. The same applies to the above-considered example with silver halides: for AgI, the ratio between the cationic and anionic radii still makes the NaCl-type structure possible, whereas in fact, the crystallization of the ZnS type takes place; that is, because of the incresing polarization interaction in AgI, the coordination number of Ag^{+} decreases in comparison with AgCl and AgBr.

The changing nature of bonding in a series of compounds of similar composition affects not only their melting points but also other properties. It has been established, for example, that the degree of dissociation of cadmium halides diminishes sharply in the series $CdCl_2 > CdBr_2 > CdI_2$. It is still lower in the case of mercuric chloride, $HgCl_2$ — even in dilute solutions, less than 0.5 per cent of the $HgCl_2$ molecules dissociate into ions. This is another proof of departure from the ionic type of bonding and transition to a molecular structure as a result of pronounced polarization interaction. It is interesting to note that compounds of Hg^{2+} with anoins that do not lend themselves readily to deformation, such as

F^-, ClO_4^-, and NO_3^-, dissociate in solutions of the same concentration almost completely — that is, they retain their ionic structure.

Since a rise in temperature promotes the polarization interaction, heating of compounds with an ionic structure leads to changes in the coordination number and increases the contribution of the covalent forces to the formation of compounds. A case in point is CsCl which usually has an ionic crystal structure with a coordination number of eight for Cs^{+}. When heated, this compound undergoes a structural change (phase change at 445 °C). As a result of the incresing mutual polarization of the ions, the coordination number goes down to six, which leads to a NaCl-type structure.

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c2) Coloration of Inorganic Compounds

Closely related to the polarization properties of cations and anions is the coloration of chemical compounds. Very often, when mutual polarization of cations and anions takes place, the formation of coloured compounds is observed. This is due to the disruption of closed (filled) electron shells as a result of polarization, with a multitude of electronic states being excited by the mutual polarization of the electronic shells of the reacting atoms.

As a rule, due to stronger mutual polarization of ions, the colour becomes more intense from fluorides to iodides in the series of halides of heavy metals. For instance, if the salt $HgCl_2$ is colourless, the iodide HgI_2 is bright red. This is a result of easier polarizability of the I^- ion as opposed to Cl^-. Interestingly, the complex mercuric iodide of composition $[HgI_4]^{2-}$ lacks colour. a possible explanation is that a polarizing effect of the mercury atom in HgI_2 involves is weaker than a similar bond in HgI_2. Owing to the less pronounced disturbance of the partner ions (atoms) due to polarization, $[HgI_4]^{2-}$ remains colourless, as is usually the case with isolated (e.g., fully hydrated) I^- and Hg^{2+} ions.

The coloration of halides of lead, silver, and other heavy metals whose electron shells are prone to deformation, changes in a similar fashion in the halogen series. For example, crystalline $PbCl_2$ is colourless, while PbI_2 has a golden sheen. Curiously, the dissolution of golden-yellow scaly crystals of PbI_2 in hot water results in a colourless solution. This must be due to a virtually complete dissociation (and probably hydration) of the Pb^{2+} and I^- ions from each other. Not being directly involved in polarization interactions, the oppositely charged Pb^{2+} and I^- ions remain colourless in solution, in a manner similar to, for example, crystalline salts KI and $Pb(NO_3)_2$ (and their solutions) where no mutual polarization of ions of any consequence takes place.

A similar pattern persists in the series "oxides-sulphides". Sulphides usually have more intense coloration than corresponding oxides. Take, for example, oxides and sulphides of the elements of Group IV of the periodic system: PbO is colourless, while PbS is black. On the other hand, hydroxides of metals usually are less intensely coloured than the corresponding oxides (derivatives of Cd^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Sn^{2+}, In^{3+}, Bi^{3+}), the most probable reason being the less pronounced deformability of the OH^- ion as opposed to O^{2-}.

For the same reason, sulphates and fluorides are less intensely coloured than hydrates and ammoniates (particularly those of Fe^{3+} and Cu^{2+}). Generally, the coloration of compounds is

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most intense when the chemically linked partners are atoms (ions) capable of exhibiting an additional polarization effect. This is why, in the periodis system, the coloration of the compounds of groups containing "trans-transition" elements ordinarily becomes more intense from top downward. A good example is provided by the colour changes in the series of sulphides of the elements belonging to Group II: ZnS is colourless, CdS is yellow, and HgS is black (because of the mercury's tendency toward additional polarization).

We have already mentioned the complex ion $[HgI_4]^{2-}$. It is colourless in aqueous solutions and solid compounds of the $K_2[HgI_4]$ type. If the weakly polarizing outer-sphere ion K^+ is substituted by a strongly polarizing cation, a coloured compound is formed. For example, $Ag_2[HgI_4]$ is yellow, and $Cu_2[HgI_4]$ is red. Apparently, the iodide ions in these compounds are as strongly affected by the cations (Ag^+ or Cu^+) as in HgI_2.

Note that the compounds $Ag_2[HgI_4]$ and $Cu_2[HgI_4]$ belong to the so-called "thermosensitive" dyes: when heated to 80-90 °C (hot water), the yellow salt $Ag_2[HgI_4]$ becomes red, while the red salt $Cu_2[HgI_4]$ turns black. The change of colour is reversible: when cooled, these substances return to the original colour they had at normal temperature. Responsible for the intensification of colour during heating is the stronger polarization associated with the greater mobility of the electron shells of atoms and ions at elevated temperature.

Thermosensitive dyes are used practically as indicators of temperature changes. For instance, when thermally unstable chemicals are commercially synthesized, the reactors are painted a dye based on thermosensitive compounds. Once a preset temperature limit is exceeded, the reactor changes in colour, and the attendant may take apprpriate measures to stop the unit from being overheated.

Reversible changes in coloration at heating are a common phenomenon in inorganic chemistry. For example, colourless ZnO and TiO_2 turn yellow when heated, then become colourless again upon cooling. When melted, colourless crystalline $InCl_3$ becomes yellow, colourless $InBr_3$ becomes light brown, and yellow InI_3 becomes dark brown.

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c3) Thermal and Redox Stability of Inorganic Compounds

It has already been mentioned that the polarization properties of atoms (ions) which are in direct contact in inorganic compounds strongly affect the redox and thermal stability of inorganic compounds. The reactions illustrating the effect of polarization characteristics of the reactants on the stability of the end product include synthesis of cupric halides. As is known, cupric chloride and bromide are rather stable. However, attempts to obtain cupric iodide in a exchange reaction, such as

$$CuSO_4 + 2\ KI \rightarrow CuI + \frac{1}{2} I_2 + K_2SO_4,$$

lead to reduction of Cu(II) to Cu(I) and to liberation of iodide. Thus, cupric iodide cannot be obtained under normal temperature conditions because of the additional polarization occuring in the Cu^{2+} - I^- system, both the cation and the anion having a loose 18-electron shell. At the same time, $CuCl_2$ and $CuBr_2$ are quite stable under similar conditions because the electron shells of Br^- and especially Cl^- are "rigid", and the additional polarization in the Cu^{2+} - Cl^- and Cu^{2+} - Br^- systems is virtually nil.

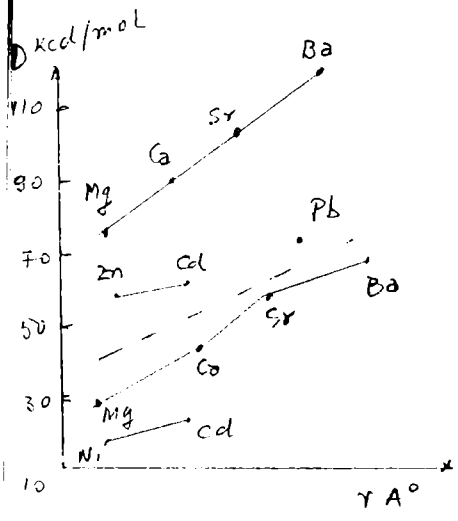

Fig. 2 Heat of dissociation of metal carbonates and sulphates (kcal/mole)

The pattern of thermal stability variations in similarly structured inorganic compounds can be traced in hydroxides of metals, various salts, and so on. The relationship between the thermal stability of carbonates and sulphates of metals, on the one hand, and the size (hence, the polarizing effect) of double-charged cations, on the other, is shown in Figure 2[1].

It can be seen that the heat of dissociation of carbonates and sulphates of alkaline-earth metals depends monotonically on the cationic radius. As regards carbonates and sulphates of transition metals, they are characterized by a rectilinear relationship but at lower temperatures. Such relationships are not typical of lead(II) salts. The abnormally low thermal stability of lead carbonate and sulphate, shown in Figure 2, is certainly due to the additional polarization effect.

The polarizing effect of the cation on the thermodynamic stability of hydroxides of metals is well illustrated by the heats of hydration of oxides of bivalent metals. For example, while

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reacting with water calcium and cadmium oxides form hydroxides of the same stoichiometric composition:

$$CaO + H_2O = Ca(OH)_2 + 16 \text{ kcal},$$

$$CdO + H_2O = Cd(OH)_2 + 3 \text{ kcal}.$$

The difference in the amount of the exoeffect is indicative of a lower thermal stability of cadmium hydroxide: Cd has an 18-electron shell, whereas Ca^{2+} has a rigid 8-electron subshell and, therefore, is immune to additional polarization, whereby its hydroxide is thermally more stable than that of cadmium.

In considering the thermal stability of hydroxides of metals, it would be appropriate to mention the low stability of such compounds as $Cu(OH)_2$, $Hg(OH)_2$, and Ag(OH). Cupric hydroxide dissociates when kept in a mother liquor in the reaction

$$Cu(OH)_2 = CuO + H_2O,$$

leaving a black residue of CuO. The hydroxides of Ag(I) and Hg(II) are not formed at all because of the extremely strong polarizing effect of Ag^+ and Hg^{2+} which have an 18-electron shell.

We should also point out the very low thermal stability of mineral acids, as compared to the salts they form. For example, the dissociation temperature of the acids H_2SO_4, HNO_3, and $HClO_4$ are relatively low, while those of their salts are much higher, especially in the case of alkali and alkaline-earth metals. Such a difference is quite natural in view of the fact that the proton (H^+), which is one of the strongest polarizers, readily weakens the chemical bonds in acids at a relatively low temperature when salts of alkali metals are still stable.

Significantly, the different polarizing effects of ions often direct chemical reactions, for example those of thermal decomposition, along different paths so that the heating the similarly structured compounds results in products of dissimilar composition. A case in point is the thermal decomposition of nitrates of alkali (8-electron shell in the cation) and transition (complete 8-electron and incomplete 18-electron shells in the cation) metals:

$$KNO_3 = KNO_2 + \frac{1}{2} O_2,$$

$$Cu(NO_3)_2 = CuO + 2\ NO_2 + \frac{1}{2} O_2,$$

$$AgNO_3 = Ag + NO_2 + \frac{1}{2} O_2.$$

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As can be seen from the above equations, the highest degree of thermal decomposition (under comparable temperature conditions) is observed in silver nitrate because the additional polarization effect is more pronounced in it than in cupric nitrate due to the greater mobility of the electron shell of silver(I) (the radius of the Ag^{+} ion is longer than that of Cu^{2+}).

The polarizing effect of the metal cation on the nitrate ion is virtually nil in potassium nitrate, which manifests itself in the detachment of one of the oxygen atoms from KNO_3 (and at a rather high temperature) without breaking the K^{+} - oxo-anion bond. If the K^{+} cation had exerted a tangible polarizing effect on the oxo-anion, then, as a result of counter polarization, the oxo-anion would have given up the oxygen atom which is predominantly acted upon by the metal cation. However, the oxide K_2O or the corresponding peroxide does not form. This is indicative of the statistical nature of the dissociation of KNO_3: heating weakens the N – O bonds in the oxo-anion, all three bonds being equivalent irrespective of whether the given oxygen atom in the NO_3^{-} anion is in direct contact with the K^{+} cation.

In the begining of this chapter we mentioned the difficulties arising when polarization concepts are applied in inorganic chemistry and the need to carefully select compounds and reactions that can be objects of discussion in terms of the polarization theory. We hope that the foregoing will convince the reader of the utility and expediency of this "polarization" approach.

IV. 2. Theoretical treatment of the covalent bond

IV. 2.1. Valence Bond (Heitler-London Theory)

A hydrogen molecule H_2 is described by a wave function $\psi = \psi_A \cdot \psi_B$ when two hydrogen atoms are brought togeter without exchanging electrons (structure I), there is a weak attraction at large distances that becomes a strong repulsion at short distances. (The hydrogen nuclei are represented as H_A and H_B and the electrons as · 1 and · 2). Since a short distances the alternative structure, in which the electrons exchange positions (structure II) is just as likely, the potential energy curve (lower solid curve) corresponds to the normal H-H distance by the echange between two equivalent structures, as in resonance stabilization.

$$I \quad H_A^{\bullet 2\circ} \quad H_B \qquad\qquad II \quad H_A^{\circ 1\bullet} \quad H_B$$

The wave functions for the individual structures can be written.

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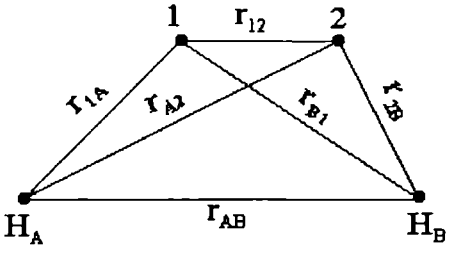
$\psi_I = \psi_A(1)\psi_B(2)$

$\psi_{II} = \psi_A(2)\psi_B(1)$

These functions must satisfy the Schrödinger equation $H\psi = E\psi$ where H isn't a simple number but a symbol which represents a sum of energies in the H_2 molecule.



$$H = \sum K.E. + \sum P.E. + \sum E.R. + EN.R.$$

$$K.E.(1) = -\frac{h^2}{2m}\left(\frac{d^2}{\partial x_1^2} + \frac{d^2}{\partial y_1^2} + \frac{d^2}{\partial z_1^2}\right)$$

$$P.E.(1) = \sum_x \frac{Z_x \cdot e}{r_{1,X}}$$

Z_X = nuclear charge of the X - atom

$r_{1,X}$ = the distance between the e_1 electron and the X nucleus.

$$E.R.(1,2) = \frac{e^2}{r_{1,2}^2} \qquad N.R.(AB) = \frac{Z_A \cdot Z_B}{r_{AB}}$$

$$H = KE(1) + KE(2) + PE(1A) + PE(1B) + PE(1B) + PE(2A) + ER(12) + NR(AB)$$

$$H = 2H_0 + H_1$$

The wave function which corresponds to this system is obtained by L.C.A.O. method as a liniar combination:

$\psi_+ = c_1\psi_I + c_2\psi_{II}$

$$\Psi_+ = c_1\Psi_A(1)\Psi_B(2) + c_2\Psi_A(2)\Psi_B(1)$$

and

$$\Psi_- = c_1\Psi_A(1)\Psi_B(2) - c_2\Psi_A(2)\Psi_B(1)$$

$$H_1\Psi = E_1\Psi$$

$$H_1\Psi_+ = E_1\Psi_+$$

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$$\int \psi_0 H_1 \psi_0 dv_1 dv_2 \quad E_1 \int \psi_0 \psi_0 dv_1 dv_2$$

$$\int (c_1 \psi_A(1) \psi_B(2) + c_2 \psi_A(2) \psi_B(1)) H_1 (c_1 \psi_A(1) \psi_B(2) + c_2 \psi_A(2) \psi_B(1)) dv_1 dv_2 =$$

$$= c_1 \psi_A(1) \psi_B(2) H_1 c_1 \psi_A(1) \psi_B(2) dv_1 dv_2 + c_1 \psi_A(1) \psi_B(2) H_1 c_2 \psi_A(2) \psi_B(1) dv_1 dv_2 +$$

$$+ c_2 \psi_A(2) \psi_B(1) H_1 c_1 \psi_A(1) \psi_B(2) dv_1 dv_2 + c_2 \psi_A(2) \psi_B(1) H_1 c_2 \psi_A(2) \psi_B(1) dv_1 dv_2$$

$c_1 = c_2 = c$ because $H_A = H_B$ in the hydrogen molecule where K corresponds to the electrostatic energy and J corresponds to the exchange energy.

$$K = \int \psi_A(1) \psi_B(2) H_1 \psi_A(1) \psi_B(2) = \int \psi_A \psi_B(1) H_1 \psi_A(2) \psi_B(1)$$

$$J = \int \psi_A(1) \psi_B(2) H_1 \psi_A(2) \psi_B(1) = \int \psi_A(2) \psi_B(1) H_1 \psi_A(1) \psi_B(2)$$

Thus $\int \psi_1 H_1 \psi_1 dv_1 dv_2 = c^2 (2K + 2J)$

$$E_1 = \frac{c^2 (2K + 2J)}{\int \psi_0 \psi_0 dv_1 dv_2}$$

$$\int \psi_1 \psi_1 dv_1 dv_2 = \int (c_1 \psi_A(1) \psi_B(2) + c_2 \psi_A(2) \psi_B(1))^2 dv_1 dv_2 =$$

$$= c_1^2 \int \psi_A^2(1) \psi_B^2(2) dv_1 dv_2 + 2 c_1 c_2 \int \psi_A(1) \psi_B(2) \psi_A(2) \psi_B(1) dv_1 dv_2 =$$

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$$c_2^2 \int \varphi_A^2(2)\,\varphi_B^2(2)\,dv_1 dv_2 = c^2[2 + 2S]$$

because $\int \varphi_A^2(1)\,\varphi_B^2(2)\,dv_1 dv_2 = \int \varphi_A^2(2)\,\varphi_B^2(1)\,dv_1 dv_2 = 1$

$\varphi_A(1), \varphi_B(2), \varphi_A(2), \varphi_B(1)$ are ortogonal functions and

$\int \varphi_A(1)\,\varphi_B(2)\,\varphi_A(2)\,\varphi_B(1)\,dv_1 dv_2 = S^2$ named the superposition integral.

$$E = \frac{(2K + 2J)c^2}{(2 + 2S^2)c^2} = \frac{2K + 2J}{(2 + 2S^2)} = \frac{K + J}{1 + S^2}$$

The $c_1 c_2$ coefficients can be determined from the maximum probability $\int \psi^2 dv = 1$.

$$c_1^2 \int \varphi_A^2(1)\,\varphi_B^2(2)\,dv_1 + c_1^2 \int \varphi_A^2(2)\,\varphi_B^2(1)\,dv_1 + 2c_1^2 \int \varphi_A(1)\,\varphi_B(2)\,dv_1 \int \varphi_A(2)\,\varphi_B(1)\,dv_1 = 1$$

$$2c_1^2 + 2c_1^2 S^2 = 1$$

$$2c_1^2(1 + S^2) = 1$$

$$c_1^2 = \frac{1}{2(1 + S^2)}$$

$c_1 = \frac{1}{\sqrt{2(1 + S^2)}}$ and $c_2 = \frac{1}{\sqrt{2(1 + S^2)}}$. The c_1, c_2 are mixing coefficients.

Similarly can be calculated the equation for $E_{II} = \frac{K + J}{1 + S^2}$ corresponds to ψ_{II}.

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The total energy: $E_{tot} = 2E_0 + E_1^+ = 2E_0 + \frac{K + J}{1 + S^2}$.

When two hydrogen atoms are brought together without exchanging electrons (structure I $H_A^{\cdot 1\,2\cdot} H_B$ there is a weak attraction at large distances that becomes a strong repulsion at short distances (dashed curve Figure 21). Since at a short distances the alternative structure, in which the electrons exchange positions (structure II $H_A^{2\cdot\ 1\cdot} H_B$), is just as likely, the potential energy curve (lower solid curve) corresponds to the normal H-H distance by the exchange between two equivalent structures (I and II) as in resonance stabilization.

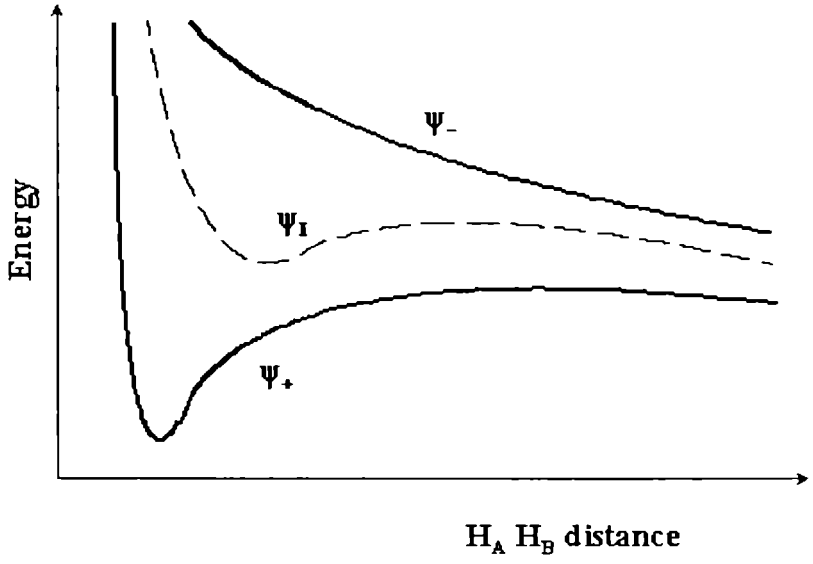

Figure 21 Potential - energy curves

The minimum in the potential energy indicates that the ψ_+ wave function leads to a stable molecule. The wave function $\psi_0 = c_1 \psi_I + c_2 \psi_{II}$ represents the situation in which no attraction is observed at any distance, because the two electrons have parallel spins (see the upper solid curve in Figure 21). Electrons must have oposed spins for favorable interaction. Pauling has shown that the results may be improved by a consideration of ionic structures for the hydrogen molecule. This results in the addition of two more terms to the wave equation.

Ionic structures	New terms to be added to the equation of ψ_+ named ψ_{ionic}
III $H_A^{(-)}:H_B^{(+)}$	
IV $H_A^{(+)}:H_B^{(-)}$	$\psi_{ion} = c_3\psi_B(1)\psi_B(2) + c_4\psi_A(1)\psi_A(2)$

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The hydrogen molecule can be characterized by a total wave function:

$$\psi_{tot} = [2\psi(1)\psi(2)]^{1/2}[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]$$

In this equation ψ_+ corresponds to ψ covalent.

The Heitler-London treatment can be extended to other molecules with the covalent bond resulting from the interaction of electrons with opposed spins on two atoms. The valence electrons of a combining atom must be unpaired. If they are not unpaired in the ground state of the atom, vacant orbitals of low energy must be available to accomodate in separate orbitals the previously spin-paired electrons.

For second-period elements the atomic orbitals must be of the same major quantum number, n, because the orbitals must not differ greatly in energy. An atom can then from a covalent bond for each of its stable valence orbitals. Thus nitrogen with the outer configuration $2s^2 2p_x^1 2p_y^1 2p_z^1$ can from three bonds, as in NF_3, but cannot from NF_5, because the second shell can accommodate only light electrons.

Phosphorus with the configuration $3s^2 3p_x^1 3p_y^1 3p_z^1$ can from PF_3; and by promoting one 3s electron to a vacant 3d orbital to give the configuration $3s^1 3p_x^1 3p_y^1 3p_z^1 3d^1$, it can from five bonds in PF_5.

The Heitler-London treatment features the formation of a chemical bond as the result of the pairing of two electrons, one form each bonded atom. The electron density of the shared pair is a maximum between the two bonded atoms. The Heitler-London treatment does not consider the formation of odd-electron molecules H_2^+, where no pairing occurs, and it doesn't include the formation of the coordinate covalent bond where one of the bonded atoms furnishes both of the electron pairs.

IV. 2.2. Valence Bond (Pauling-Slater) Theory Overlap of Atomic Orbitals

The main consideration is that stable compounds result from the tendency to fill all stable orbitals with electron pairs, shared or unshared.

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A covalent bond may be described as resulting from the overlap of orbitals on two atoms so that the two orbitals can be occupied by an electron pair. In HF the spherically simmetrical s orbital of H overlaps with the singly occupied 2p orbital of F.

The shape of a molecule is determireed primarily by the directional characteristics of the orbital involved. But there are many molecules (e.g. H_2O, NH_3) which do not obey the bond angle of the involved orbitals. For example the H_2O molecule results from the overlap of the two singly-occupied p orbitals of oxygen with the s orbital of each of two hydrogen atoms, to from an angular molecule (see Figure 22a). The p orbitals are mutually perpendicular, but the bond angle in water is 104.45^0. Repulsion between the hydrogen atoms only, doesn't accounts for the fact that the angle is greater than 90^0. The ammonia molecule is pyramidal with a bond angle of 107.3^0, while the three p orbitals of the nitrogen atom are mutually perpendicular. In the methane CH_4 molecule the outer configuration of the carbon atom must be $2s^1 2p_x^1 2p_y^1 2p_z^1$ and no $2s^2 2p_x^1 2p_y^1$. These characteristic aspects of the molecules can be explained by means of the by hybridization theory.(Pauling-Slater).

Hybridization

The process of combining atomic orbitals to give mixed orbitals is known as hybridization. In the second period there are four kind of combining **s** an **p** orbitals.

(i) The combination of the **s** and three **p** orbitals gives tetrahedral hybrid $\mathbf{sp^3}$ orbitals. The **p** lobe with the same sign of the ψ function as that of the **s** orbital is enlarged, and the one of opposite sign is diminished. The enlarged lobe of the resulting orbital can give more favorable overlap with the orbital of another atom and thus from a stronger bond than can either the **p** or **s** orbitals alone. The orbital represented is one of the four equivalent $\mathbf{sp^3}$ orbitals.

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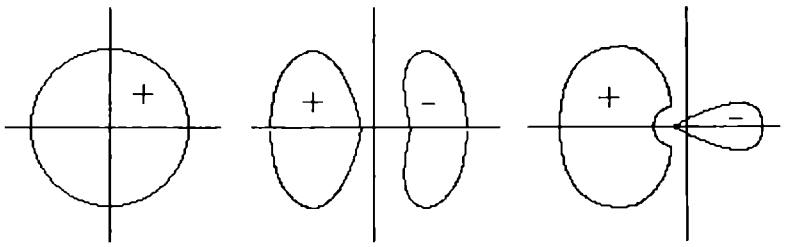

s p sp^3

(ii) There are three equivalent sp^2 hybrid orbitals and

(iii) two equivalent **sp** orbitals.

The shapes of the major lobes sp^3, sp^2, **sp** hybrid orbitals differ very little, mainly in the relative sizes of the minor and major lobe. The minor lobe is largest for sp^3 and smallest for **sp**, so the greatest fraction of electron density would be in the bonding lobe for the **sp** hybrid orbital. Overlap integrals increase in the order $sp^3 < sp^2 < sp$, indicating the greatest overlap for **sp** bonds. The increasing C-H bond energies in the series CH_4,C_2H_4, C_2H_2 support increasing bond strengths with increasing s character for sp^2 hybrid - that is, greatest for **sp**.

Pauling used the extension of the orbitals, rather than the overlap integrals, to arrive at a different order of relative bond strengths: 1.93 for **sp**, 1.99 for sp^2, 2.00 for sp^3, compared with 1.00 for pure **s**. The overlap integrals provide better estimates of bond strengths.

Figure 23 displays some of the important hybrids - including cases involving **d** orbital participation - along with the corresponding geometrical configurations.

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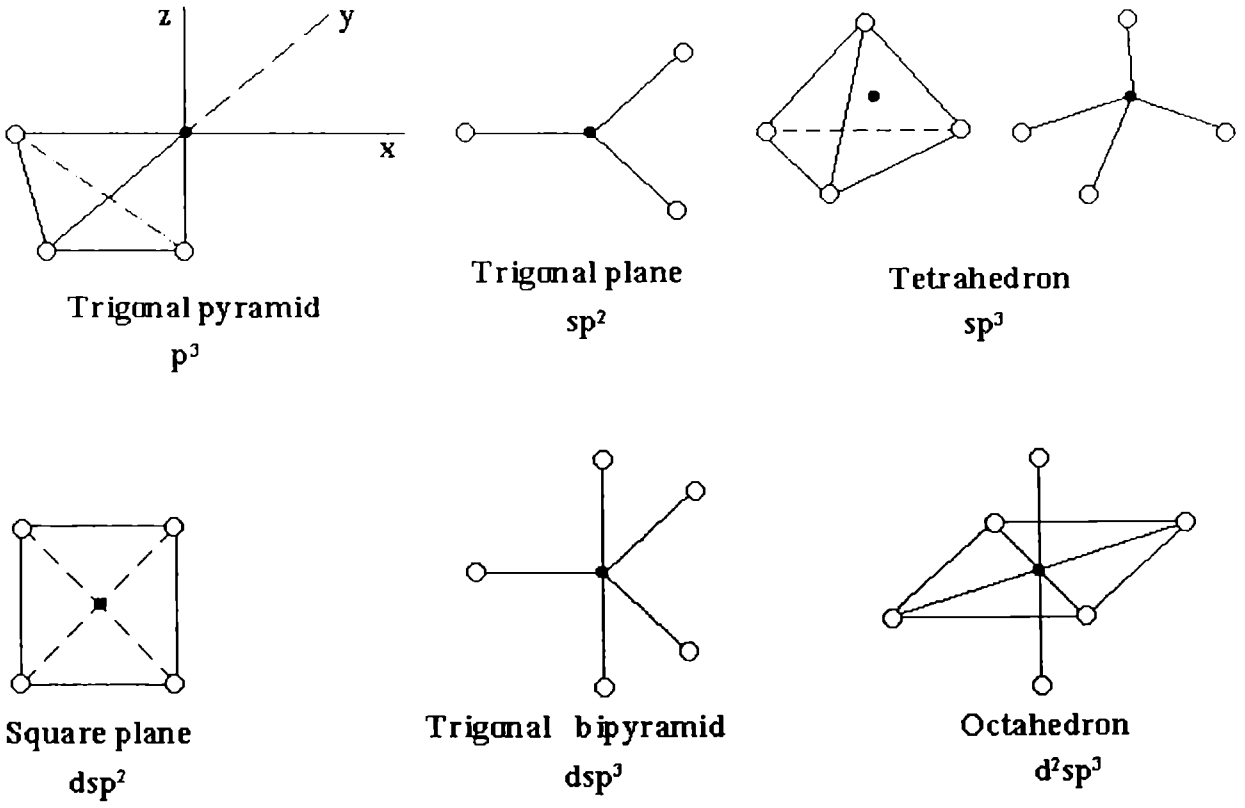

Figure 23 Some bonding configuration

IV. 2.3 Shapes of Molecules. Molecular Geometry and Hybridization

The shape of a molecule, to a first approximation, is determined by its σ bond structure. Since they often occupy hybridized orbitals, unshared electron pairs, can be treated as bouded groups in determining the hybridization: accordingly, the hybridization in NH_3 and H_2O can be considered to be **sp^3**. The importance of unshared electron pairs in determining molecular shapes is illustrated in Table IV.2.

Table IV.2 Shapes of some simple molecules

General Formula	Number of Unshared Electrons on A	τ Bonding Orbital Hybridi-zation	Shape	Examples

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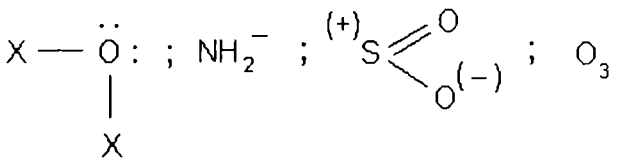
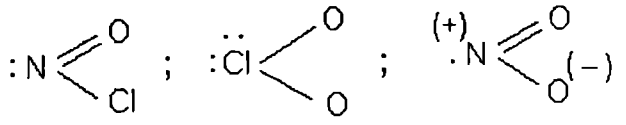
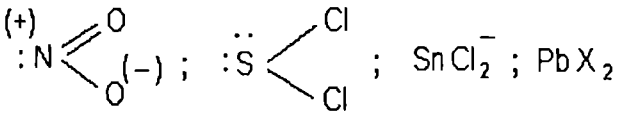
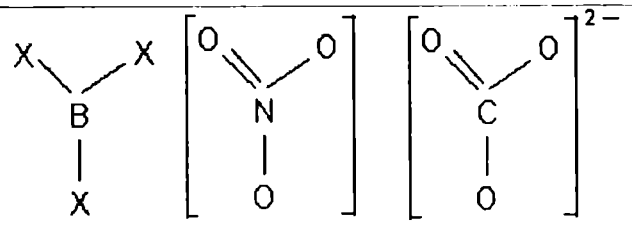
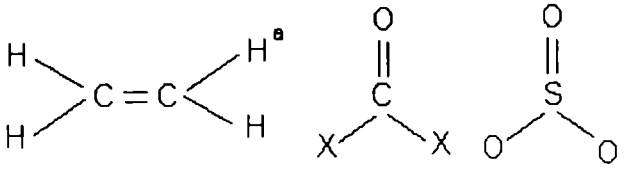
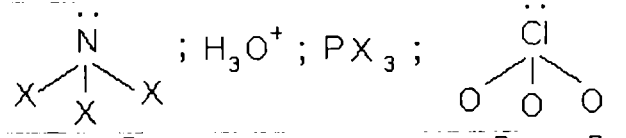
AX_2	none	sp	Liniar	O=C=O; S=C=S; O=N'=O; H-C≡N; CH≡CH; ZnX_2; CdX_2; $AgCl_2^-$; HgX_2
	one or more	sp^2 or sp^3	Angular	
				
				
AX_3	none	sp^2	Planar	
				
	one or two	sp^3	Pyramidal	
AH_4	none	sp^3	Tetra-hedral	CX_4; NH_4^+; BX_4^-; SiX_4; TiX_4; ZnX_4^{2-}; SO_4^{2-}; SO_2Cl_2; POX_3; PO_4^{3-}; ClO_4^-

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In many molecules it is difficult to assess a priori the relative importance of various contributing structures or the contribution of a particular type of hybridization. Atoms with more low-lying orbitals than valence electrons will have reasonably unambigous σ bond configurations and hence predictable structures. Atoms with more valence electrons than low-lting orbitals may contribute these electrons in varying degrees in diverse situation, and accordingly, may have several distinct and not easily available σ bond structures. For example in trimethoxoboron, $B(OCH_3)_3$, molecule the boron hybridization must be **sp²** with bond angles 120°, but the orbital hybridization of the oxygen must be intermediate between **sp³**and **sp²** (Figure IV.9). Hence double bonding would favor **sp²** hybridization here. Similarly the P-N bond in H_2N-PH_2 might be **sp²**, **sp³** or some intermediate combination of N orbitals. The hybridization of the σ bonding orbitals of each nitrogen in N_2O_5 must be **sp²**, but the bridging oxygen might be **sp³**, **sp²**, or even **sp**.

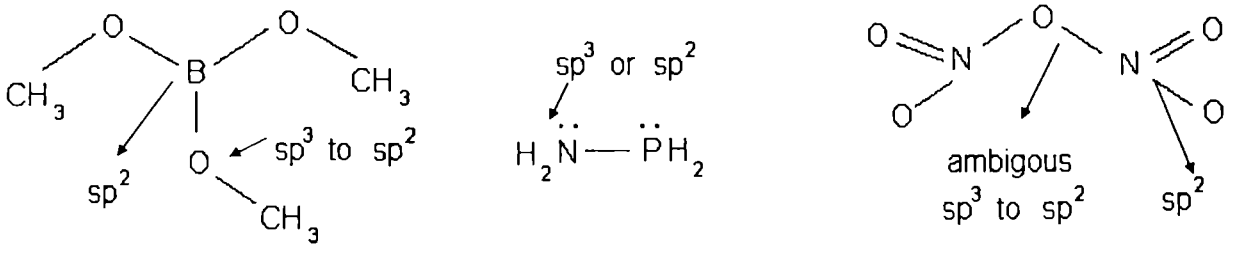

Figure IV.9 - Possible assignments of hybridization

The geometry of a molecule in an excited electronic state likely will differ drastically from that of the ground state, as the promotion of an electron can charge the hybridization of the orbitals.

IV. 2.4. The Pauli Exclusion Principle and the Prediction of the Shapes of Molecules (Valence Shell Electron-Pair Repulsion Theory)

You can predict the approximate shapes of simple molecules by considering unshared electron pairs (lone pairs) to be equivalent to bonded groups. To obtain more exact descriptions of the molecular shapes and variations of bond angles, you must take into account repulsion among electron pairs in the valence shell of the central atom. Repulsion between bonding pairs is not as great as repulsion between lone pairs. This approach was introduced by Gillespie and

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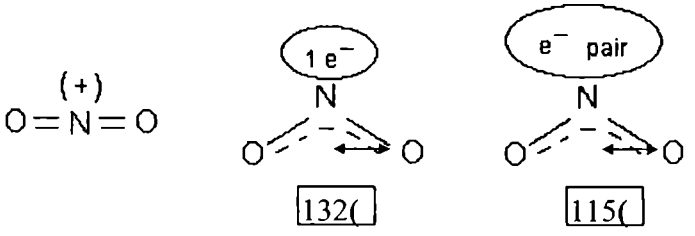
Nyholm and developed extensively by Gillespie as the valence shell electron pair repulsion (VSEPR) theory.

If one of the electron pairs is used for bonding, as in HF, the four pairs are no longer equivalent. The bonding pair now becomes more localized, since its electrons are restricted in their motion by two positive nuclei. If two electron pairs are used for bonding, as in H_2O, the bond angle will be determined by the repulsions among the four electron pairs. Instead of the normal tetrahedral angle (109.47^0) for four equivalent pairs, as found in CH_4 and as expected for O^{2-}, the bond angle in H_2O is 104.45^0.

The repulsion between electron pairs decreases in the order

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

In NH_3 the HNH bond angles are 107.3^0 - an angle greater than that in H_2O because there are no lone pair-lone pair repulsions.



NO_2^+ NO_2 NO_2^-

Figure IV.10 - Bond angles in NO_2^+, NO_2, NO_2^-

Comparing the bond angles in NO_2 (132^0) and in NO_2^- (115^0) demonstrates that a single unshared electron causes less repulsion than an unshared electron pair. The nirtyl ion, NO_2^+, with no unshared electron on nitrogen, is linear (see Figure IV.10).

The non angles decrease in the series NH_3, PH_3, AsH_3, SbH_3 and in the series H_2O, H_2S, H_2Se, H_2Te (see Table), presumably because the increasing size and lower electronegativity of the central atom permit the bonding electrons to be drawn out further, thus decreasing the repulsion between bonding pairs. The variation in bond angles is in the direction expected for are increase in the bonds' **p** character: that is, the bond angles approach the values expected for $\mathbf{p^3}$ bonds, rather than those for $\mathbf{sp^3}$ hybrid bonds. This is just the opposite of what might be expected, since the energy difference between the **s** and **p** orbitals is greatest for nitrogen.

The bond angles decrease by large amounts from NH_3 to PH_3 or from H_2O to H_2S, then by very small amounts for the following members of each series.

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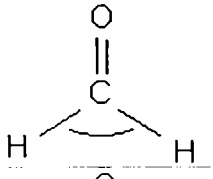
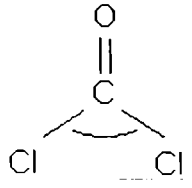
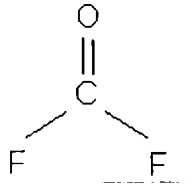
Gillespie suggests thant the difference arises because N and O are memberes of the second period, for which the octet represents a closed shell. Strong repulsions between the electron pairs result from the fact that the space around the central atom is filled completely. For compounds of elements of the second period, the bond angles realely fall below the tetrahedral angle by more than a few degrees. Members of the later periods can accomodate more than four electron pairs in the valence shell; the maximum usually is six pairs. Six electron pairs in the valence shell of an atom should produce an octahedral arrangement with angles of 90^0 between electron pairs, and the bond angles of the hydrides of the heavier group V and VI elements do seem to approach 90^0 (see Table 6).

The decrease in the bond angles for NF_3 and F_2O as compared with NH_3 and H_2O may be explained in terms of the decrease in repulsion between bonding pairs resulting from the electrons being drawn out further by the fluorine. The FCF bond angles in the C-F compounds shown in the Table IV.3 are also smaller than HCH bond angles in the corresponding C-H compounds. The bond angles of the fluorine compounds are smaller than those of the corresponding hydrogen compounds only for second-period elements.

Table IV.3 Comparison of bond angles

CH_4		109.47^0		
CH_3F	HCH	110^0		115.8^0
CH_3Cl	HCH	110.3^0		
CHF_3	FCF	108.8^0		111.3^0
$CHCl_3$	ClCCl	110.4^0		108.0^0

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NH_3	107.3^0	NF_3	102.4^0	NCl_3	106.8^0	Pbr_3 101.0^0
PH_3	93.3^0	PF_3	97.8^0	PCl_3	100.1^0	PI_3 102^0
AsH_3	91.8^0	AsF_3	96.2^0	$AsCl_3$	98.5^0	
SbH_3	91.3^0	SbF_3	95.0^0	$SbCl_3$	97.2^0	

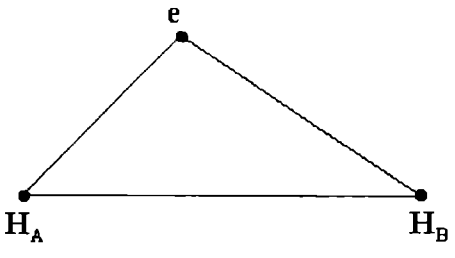
IV. 3. Molecular orbital theory of covalent bonding

In (V.B.T) electron pairs are localized between particular pairs of nuclei, and the wave function for these electrons are just the products of atomic wave functions.

The M.O. theory in building up a multielectron atom started with a nucleus and a set of one-center orbitals about that nucleus and fed the required number of electrons into these orbitals by solving exactly the problem with only one electron and then assumed that ehen many electrons are present the orbitals have the same form but that their relative energies are affected by the shielding of one electron by another. In other words, we treat each electron as if it moves in the effective field produced by the nucleus and all of the other electrons.

The LCAO method is a simple and qualitatively useful approximation. To develop this idea more concretely we shall use the hydrogen molecule ion H_2^+. This is a prototype for homonuclear diatomic molecules just as the hydrogen atom is for atoms in general.

If the electron belonged to either of hydrogen nuclei A or B alone, its behavior in the ground state would be described by ϕ_A or ϕ_B alone. When it is in some general position with reference to the nuclear frame work it can be approximately described by a superposition of both, that is, by $\Phi_A \pm \Phi_B$. Such an algebraic sum of functions is called a linear combination. The two normalized LCAO wave functions written out fully, are H_2^+.



$$\psi_b = c_1 \psi_A + c_2 \psi_B$$

$$\psi_a = c_1 \psi_A - c_2 \psi_B$$

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$$H \square \square E \square$$

$$\square H \square \square E \square^2$$

$$\square \square H \square dv \square E \square \square^2 dv$$

$$\square_b H \square_b dv \square E \square \square_b^2 dv$$

$$E_b \square \frac{\square \square_b H \square_b dv}{\square \square_b^2 dv} \square \frac{\square \square c_1 \square_A \square c_2 \square_B \square H \square c_1 \square_A \square c_2 \square_B \square dv}{\square c_1^2 \square_A^2 \square 2c_1 c_2 \square_A \square_B \square c_2^2 \square_B^2 \square dv} \square$$

$$\square \frac{c_1^2 \square \square_A H \square_A dv \square c_1 c_2 \square \square_A H \square_B dv \square c_2 c_1 \square \square_B H \square_A \square c_2^2 \square \square_B H \square_B dv}{c_1^2 \square \square_A^2 dv \square 2c_1 c_2 \square \square_A \square_B dv \square c_2^2 \square \square_B^2 dv} \square$$

$$\left.\begin{array}{l} \square \square_A H \square_A dv \square H_A \\ \square \square_B H \square_B dv \square H_{BB} \end{array}\right\} \text{coulombien integrals}$$

$$\left.\begin{array}{l} \square \square_A H \square_B dv \square H_{AB} \\ \square \square_B H \square \square_A dv \square H_{BA} \end{array}\right\} \text{change integrals}$$

$$\left.\begin{array}{l} \square \square_A^2 dv \square S_{AA} \\ \square \square_A \square \square_B dv \square S_{AB} \\ \square \square_B^2 dv \square S_{BB} \end{array}\right\} \text{the overlap integrals}$$

$$E_b \square \frac{c_1^2 H_{AA} \square 2c_1 c_2 H_{AB} \square c_2^2 H_{BB}}{c_1^2 S_{AA} \square 2c_1 c_2 S_{AB} \square c_2^2 S_{BB}}$$

In variational method $\frac{\partial E}{\partial c_1} \square 0$ and $\frac{\partial E}{\partial c_2} \square 0$

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$$2c_1H_{AA} + 2c_2H_{AB} - E(2c_1S_{AA} + 2c_2S_{AB}[$$
$$2c_2H_{BB} + 2c_1H_{AB} - E(2c_2S_{BB} + 2c_1S_{AB})$$

$$c_1(H_{AA} - ES_{AA}) + c_2(H_{AB} - ES_{AB}) = 0$$
$$c_1(H_{AB} - ES_{AB}) + c_2(H_{BB} - ES_{BB}) = 0$$

The solutions of the system are nonzero if

$$\begin{vmatrix} H_{AA} - ES_{AB} & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

The solutions of the system are obtained after two succesively aproximations regart to

(i) $S_{AB} = 0$

and

(ii) $S_{AB} \neq 0$

The overlap between a pair of atomic orbitals, S, is given by the equation $S = \int \psi_A \psi_B \, d\tau$ and S is called the overlap integral. This integral may have a value which is positive, negative or exactly zero. When its value is positive, there is a built-up of electronic charge between the nuclei and bond can be formed. When the overlap integral is negative, there is a reduction in the electron density between the nuclei. This increases the repulsion between them and they tend to move aport. When the overlap is zero, there is no net interaction, attractive or repulsive.

Examples are presented in Figure 26. The overlaps shown in (a) -(d) are all positive, in (e) - (h) are negative while those in (i) - (l) are zero.

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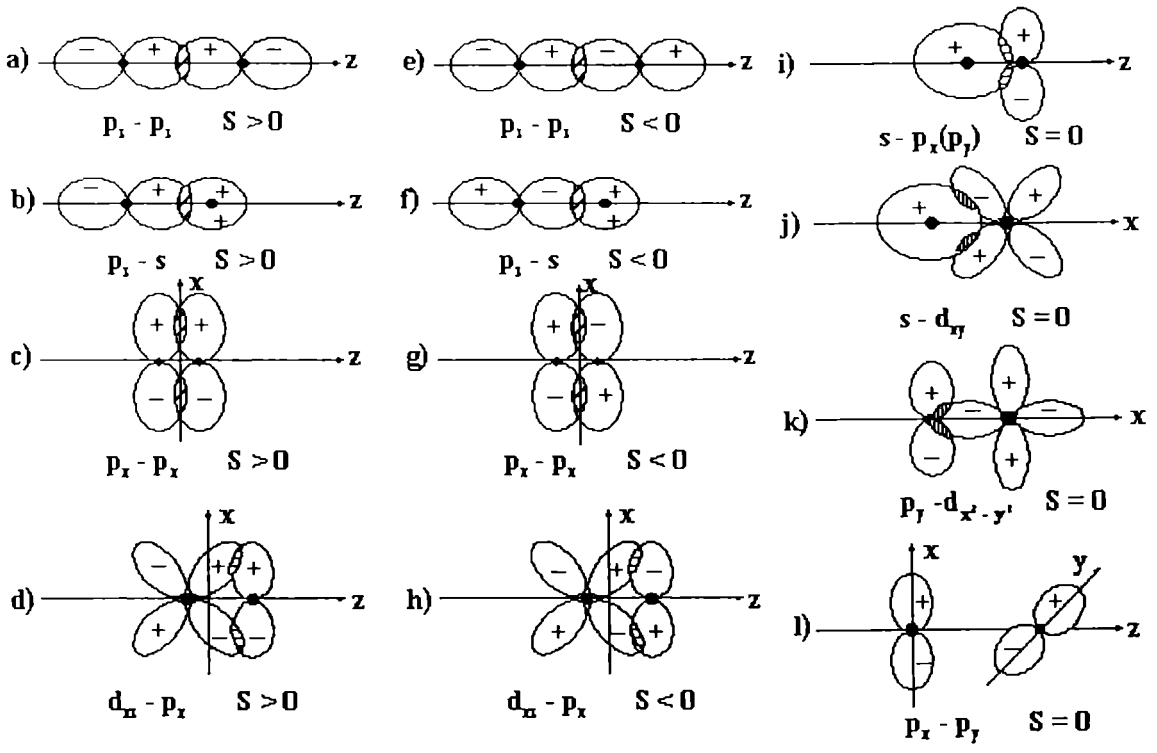

Figure 26 - Some reprezentative positive, negative and zero overlaps

It is often desirable to estimate the magnitude of S. This can be done by expressing Ψ_A and Ψ_B in equation: $S = \int \Psi_A \Psi_B \, d\tau$ and carrying out the integration. Usually it is used the radial factor R(r) of the Ψ_A and Ψ_B, which were proposed many years ago by Slater.

$$R(r) = N r^{n-1} e^{-\mu r / a_H}$$

where **N** is a normalizing factor, **n** is the principal quantum number, $\mathbf{a_H}$ is the Bohr radius and $\boldsymbol{\mu}$ is a function of the effective nuclear charge for an electron in the orbital concerned.

Orbitals which use the usual angular factors obtained by solving the wave equation for hydrogen together with these simple radial functions are called Slater-Type Orbitals (STO's). The overlaps computed using single STO's are rough approximations by comparison with Hartree-Fock method.

However, it is possible to take linear combinations of a few STO's so as to approximate very closely the true shape of an orbital (Figure 27)

In H_2^+ molecule in the first approximation. (i) $S_{AB} = 0$; $H_{AA} = H_{BB} = \alpha$

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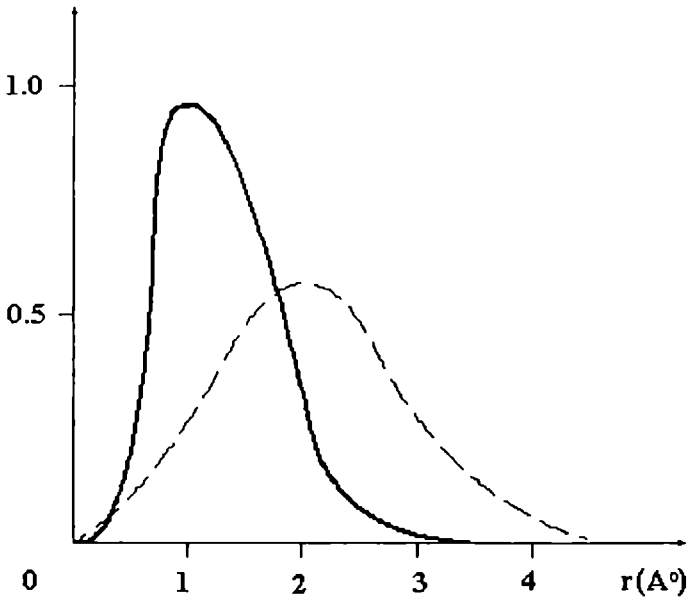

Figure 27 - A comparison of a Hartree-Fock 3d wave function for the Cr^{3+} ion with a Slater Type wave function

(A and B are identically atom)

$S_{AA} = S_{BB} = 1$ (for ortogonale functions)

$H_{AB} = H_{BA} = \beta$

$$\begin{vmatrix} \square\square E & \square \\ \square & \square\square E \end{vmatrix} = 0$$

$\alpha^2 - 2E\alpha + E^2 - \beta^2 = 0$

$E^2 - 2\alpha E + \alpha^2 - \beta^2 = 0$

$(E - \alpha)^2 - \beta^2 = 0$

$(E - \alpha - \beta)(E - \alpha + \beta) = 0$

$E_b = \alpha + \beta$

$E_a = \alpha - \beta$

For $E_b = \alpha + \beta$

$c_1(\alpha - E_b) + c_2\beta = 0$

$c_1(\alpha - \alpha - \beta) + c_2\beta = 0$

$c_1(\alpha - \alpha - \beta) + c_2(\alpha - \alpha - \beta) = 0$

$\Rightarrow c_1 = c_2$

For $E_a = \alpha - \beta \Rightarrow c_1 = -c_2$

We know that Ψ_A and Ψ_B are orthonormale functions and

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$\int \psi_A \psi_B \, d\tau = 1 \qquad A = B$

$\int \psi_A^2 \, d\tau = 1$

$\psi_a = c_1\phi_A + c_2\phi_B$

$c_1^2 \int \phi_A^2 \, d\tau + 2c_1c_2 \int \phi_A\phi_B \, d\tau + c_2^2 \int \phi_B^2 \, d\tau = 1$

$S_{AA} = 1 \qquad S_{AB} = 0 \qquad S_{BB} = 1$

$c_1^2 + c_2^2 = 1$ but $c_1 = c_2$ for E_b

$2c_1^2 = 1 \qquad c_1 = c_2 = \frac{1}{\sqrt{2}}$

and $c_1 = - c_2$ for E_a

$c_1 = \frac{1}{\sqrt{2}}$ and $c_2 = - \frac{1}{\sqrt{2}}$

$\psi_b = \frac{1}{\sqrt{2}} (\phi_A + \phi_B)$

$\psi_a = \frac{1}{\sqrt{2}} (\Phi_A - \Phi_B)$

In order to ulinesnderstand the physical mearing of the two LCAO- MO's ket us first examine Figure 28. The solid lines show ψ_a^2 and ψ_b^2, the squares being used because we are at the moment chiefly interested in how the electron density is distributed along the internuclear line. The dotted lines show the electron density in the individula atomic orbitals, that is, they show Φ_a^2 and Φ_b^2. As a further indication of the significance of ψ_a^2 and ψ_b^2, they may also be compared with the dashed line, which is a plot of $\sqrt{1/2}\ \Phi_a^2 + \sqrt{1/2}\ \Phi_b^2$. This function gives the distribution of one electron spending its time equally in Φ_A and Φ_B, these remaining, however, as separate atomic orbitals. The factors of $\sqrt{1/2}$ normalize the total electron density in each Φ to 1/2. The subscript **b**, mearing bonding, and the subscript **a**, mearing antibonding.

Now the integral α is obviously just the energy of an electron in the orbital Φ_A or Φ_B , that is, it is equal to the ground state energy of the hydrogen atom. The integral β represents the

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energy of interaction between the orbitals Φ_A and Φ_B. It is called an exchange integral or resonance integral, and it can be shown that it is inherently negative. Thus an electron occupying the bonding MO, Ψ_b, is more stable and an electron in Ψ_a is less stable than one in a pure atomic orbital, Φ_A or Φ_B. The actual energies os stabilization and destabilization can be obtained in units of β by inserting the normalization coefficients.

If we make the approximation that overlap can be ignosed, so that $c_1^2 = c_2^2 = 1/2$, we find that:

$$E_a = \alpha + \beta \quad \text{and} \quad E_b = \alpha - \beta$$

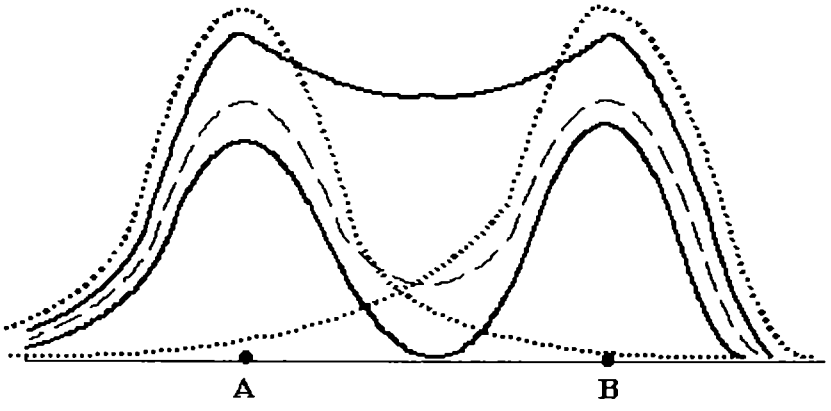

Figure 27

(.....) ϕ_A^2, ϕ_B^2 The atomic orbital electron probabilities

(—) ψ_a^2 and ψ_b^2 the molecular orbital electron probabilities

(---) distribution of a single electron equally distributed over ϕ_A and ϕ_B along the intermolecular line for H_2^+. including overlap

These results are expressed in the energy level diagram, Figure 29. The atomic orbitals of the constituent atoms are placed on each side, and the resulting MO's are placed in the center. It is to be noted that when the overlap is included in the normalization coefficients, the problem becomes more complicated algebraically and the energy level diagram no longer possesses the simple, symmetrical form of Figure 29.

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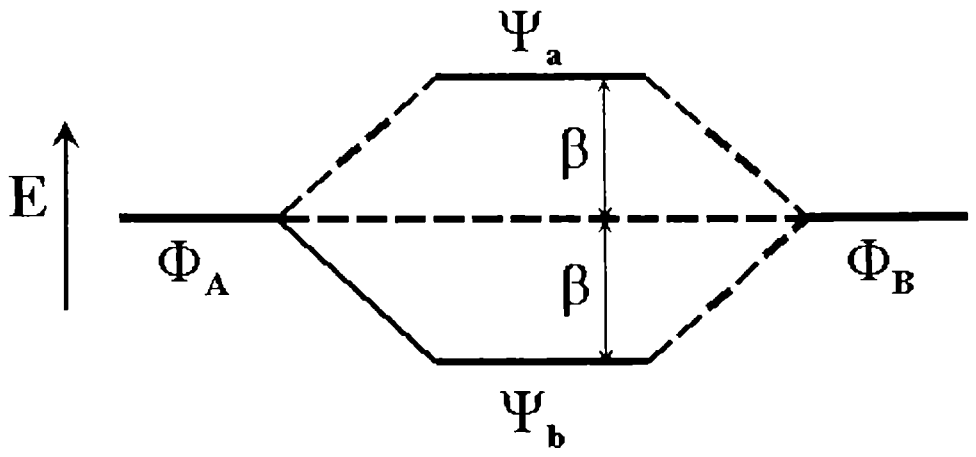

Figure 29 - Energy level diagram showing the formation of bonding and antibonding MO's from two equivalent atomic orbitals in a homonuclear diatomic molecule

In general, the larger the value of S for two orbitals Φ_A and Φ_B on two atoms, the stronger would be the bond which is formed using these orbitals.

Mulliken proposed that integrals β should be roughly proportional to the corresponding overlap integrals. It is also necessary to build into the relation expressing this proportionality a dependence on the overage value of the energies of the orbitals which are forming the bond. Thus the following general equation is written:

$$\int \Phi_A H \Phi_B \, d\tau = \beta = C \, \beta_{av} S = C \, \beta_{av} \int \Phi_A \Phi_B \, d\tau$$

$$\beta_{av} = (\beta_A + \beta_B)/2$$

or $\beta_{av} = (\beta_A \times \beta_B)^{1/2}$

geometrical overage $C \cong 2.0$.

Bond Orders : The bond order is defined in MO theory as the number of electron pairs occupying bondingt MO's minus the number of electron pairs occupying antibonding MO's.

IV. 3.1 Homonuclear Diatonic Molecules

The kind of MO are illustrated in Figure IV.20

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σ (sigma) MO has a cylindrical symmetry about the internuclear axis. A π-type orbital is one whose nodal plane includes the molecular oxis.

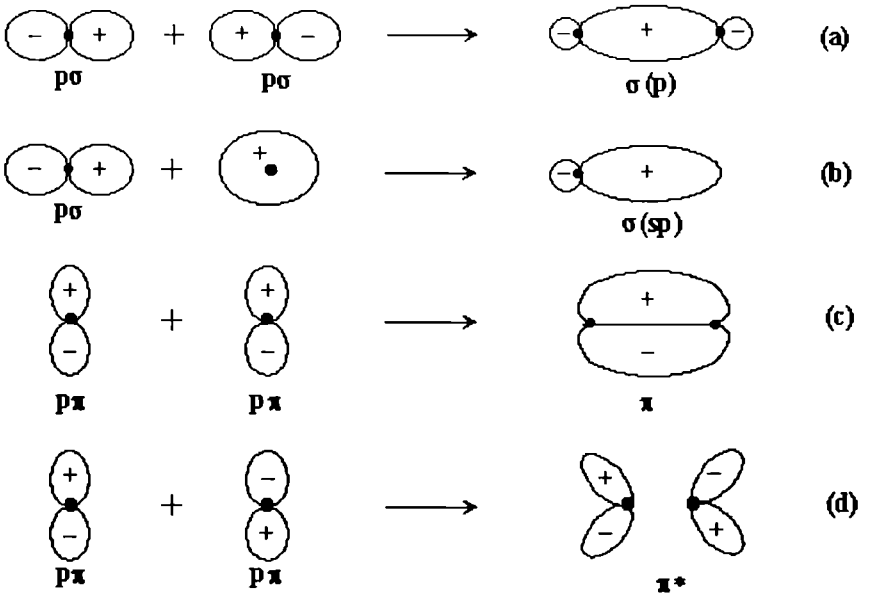

Figure IV.20 - Diagrams illustrating the formation of some simple tw-center MO's from atomic orbitals

We may begin by treating the three types of orbitals **s**, $\mathbf{p}_\sigma$ and $\mathbf{p}_\pi$ entirely separately. Thus the **s** orbitals give rise to σ_s and σ_s^*, bonding and antibonding MO's, respectively. The two $\mathbf{p}_\sigma$ orbitals combine to give σ_p and σ_p^* MO's. The $\mathbf{p}_x$ and $\mathbf{p}_y$ orbitals on each atom are of the same energy and form two π-type bonding MO and two π^*-type antibonding MO. The two MO's of each pair are said to be degnerate.It is found that the magnitudes of the three sorts of overlaps decrease in the order S-S ≈ p_σ - p_σ > p_π - p_π, and the corresponding values of β should also decrease in the same order. On the basis of these considerations for the elements of the first short period the **p** orbitals have higher energies than the **s**

orbitals, the energy level diagram shown in Figure IV.21*a* can be drawn. However, this diagram ignores one factor in the problem and is therefore not entirely correct. We have assumed that the **s** orbitals interact only with one another and the $\mathbf{p}_\sigma$ orbitals only with one another. It is wrong to neglect entirely the other interactions permitted by symmetry. Actually there are interactions between **s** and $\mathbf{p}_\sigma$ orbitals (see Figure IV.21*b*). As a result of the mixing of **s** and **p** character in all

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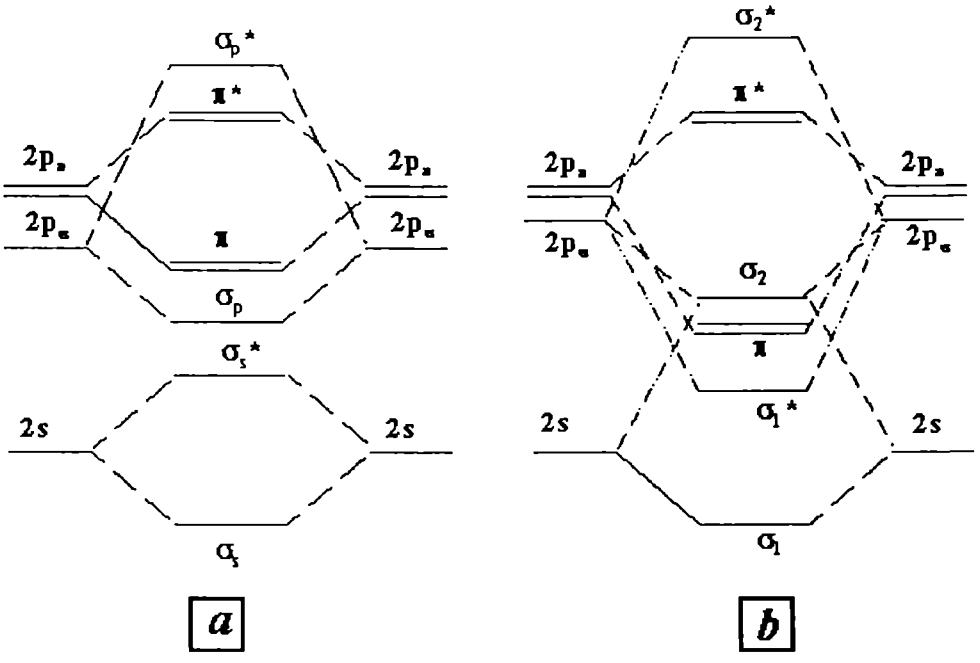
the σ MO's, their energies are shifted such that the lower two become more stable while the upper two become less stable.

Figure IV.21 - Schematic energy level diagrams showing how atomic orbitals of two (identical) atoms of the first short period to form molecular orbitals



Now, referring to Figure IV.21*a* we see that if these shifts are sufficiently large, there may be a charege in the qualitative order of the levels, namely, the 3-rd lowest orbital may be a π orbital instead of a σ orbital as shown in Figure IV.21*b*. The extent of the energy shifts will be greatest when the energy difference between the s and p orbitals is least because then they can interact most. The **s - p** energy difference is relatively small for Li (≈ 2 eV) and increases steadily until it is about 27 eV for Ne. Thus, while we might definitely expect the pattern shown in Figure IV.21*b* at the beginning of the period, the pattern in Figure IV.21*a* a might be correct at the end (i.e. for F_2). On the basis of experimental data, the pattern in Figure IV.21*b* does appear to persist as for, at least, as N_2.

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We shall now consider the electron configurations of each of the homonuclear diatomic molecules of the elements in the first short period on the basis of the LCAO-MO theory outlined above.

Li_2 $(\sigma_1)^2$ the bond order (B.O) = $\frac{2}{2} = 1$

diamagnetic molecule

Li — Li 2.67 A° and H — H 0.74 A°

E_{Li-Li} 25 kcal/mol; E_{H-H} 103 kcal/mol.

Two factors account for these differences. First, the **2s** and **2p** orbitals of Li are much larger and more diffuse than the **1s** orbital of hydrogen. Thus they tend to overlap less effectively and with maximum overlap at a greater internuclear distance than in the case of the hydrogen 1s orbitals. Second, the electrons occupying the **1s** shells of the Li atoms cause a repulsion between the atoms.

Be_2 $(\sigma_1)^2 (\sigma_1^*)^2$ B.O = $\frac{2-2}{2} = 0$ Be_2 has not been observed

B_2 $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^2$ on the basis of Figure 31*b*

$(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^2$ on the basis of Figure 31*a*

Experiment shows that B_2 has two unpaired electrons in a π orbital; thus Figure IV.21*b* is still correct at B_2.

B.O. = $\frac{4-2}{2} = 1$ (one net π bond, since the σ interactions cancel).

C_2 For this molecule the level order in Figure IV.21*b* predicts a configuration $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^4$, while that the event that the σ_2 and π levels are very close, a $(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^1 (\pi)^3$ configuration is also possible.

The latest experimental results indicate that the ground state is derived from $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^4$ configuration although a state derived from the $(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^1 (\pi)^3$ configuration lies only ≈ 610 cm^{-1} higher. B.O = 2 is in according to bond energy of 150 kcal/mol.

N_2 For N_2, with a very high bond energy (225 kcal/mol) and no unpaired electrons,

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either of the copnfigurations $(\sigma_1)^2\ (\sigma_1^*)^2\ (\pi)^4\ (\sigma_2)^2$ or $(\sigma_1)^2\ (\sigma_1^*)^2\ (\sigma_2)^2\ (\pi)^4$ would be acceptable, each giving a B.O = 3. That the former is actually correct by the fact that the odd electron in N_2^+ is in a sigma orbital according to spectroscopic evidence.

O_2 For this molecule the electron configuration might be either $(\sigma_1)^2\ (\sigma_1^*)^2\ (\sigma_2)^1\ (\pi)^4\ (\pi^*)^2$ or$(\sigma_1)^2\ (\sigma_1^*)^2\ (\pi)^4\ (\sigma_2)^2\ (\pi^*)^2$ .B.O.= 2 and two unpaired electrons are expected. Both these predictions are in good accord with experiment, the experimental bond energy being 118 kcal/mol. It is also interesting to note that the addition of electrons to O_2 causes the bond length to increase (d_{O2}=1.21 A°; d_{O2^-} = 1.26 A°; $d_{O2^{2-}}$ = 1.49 A°) while the loss of an electron causes the bond to shorten (d_{O2^+} = 1.12 A°).

These results are therefore in excellent accord with the MO electron configuration, since the orbital to or from which electrons are added or removed is an antibonding one. In O_2^+ B.O. = 2.5 and in O_2^{2-} B.O. = 1.

F_2 On adding two more electrons to the O_2 configuration we fill all orbitals except σ_2^* B.O. = 1.

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V. FURTHER PROPERTIES OF ATOMS, MOLECULES AND CHEMICAL BONDS

V. 1. Bond Energies

For a diatomic molecule the bond energy, **D**, is equal to the enthalpy of the reaction

$$XY_{(g)} = X_{(g)} + Y_{(g)} \qquad \Delta H = D$$

where the molecule and the atoms are all in their ground states. The bond energy is a function of temperature, and the best value to use would be that for the hypotheoretical reaction at O^0K. An Ab_n type molecule where all B's are equivalently bonded to A (i.e. BF_3) all B-F bond energies, $D_{B\text{-}F}$, must be equal and the relation:

$$BF_{3\,(g)} = B_{(g)} + 3\ F_{(g)} \qquad \Delta H = 3\ D_{B\text{-}F}$$

is obvious. Thus if we know the heats of formation of $BF_{3\,(g)}$, $B_{(g)}$ and $F_{(g)}$ we can readily calculate $D_{B\text{-}F}$. This vaqlue is called the mean thermochemical bond energy. However, it is not the energy, ΔH_1, of the process.

$$BF_{3\,(g)} = BF_{2\,(g)} + F_{(g)} \qquad \Delta H_1$$

since when the first bond is broken, the nature of the remaining two will necessarily be altered to some extent. Also ΔH_2 and ΔH_3

$$BF_{2\,(g)} = BF_{(g)} + F_{(g)} \qquad \Delta H_2$$

$$BF_{(g)} = B_{(g)} + F_{(g)} \qquad \Delta H_3$$

are not likely to be equal to one another, or to ΔH_1. It is of course, true that

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = 3\ D_{B\text{-}F}$$

because the Hess'law can be applied

There are many molecules in which two or more different kinds of bonds exist. In C_2H_6 for example:

$$C_2H_6 = 2\ C_{(g)} + 6\ H_{(g)} \qquad \Delta H = 6\ D_{C\text{-}H} + D_{C\text{-}C}$$

we must know one of the two unknows $D_{C\text{-}C}$ or $D_{C\text{-}H}$. We may evaluate a mean C-H bond enery in methane since there are enough experimental data to tell us the energy of the process:

$$CH_{4\,(g)} = C_{(g)} + 4\ H_{(g)} \qquad \frac{1}{4}\ \Delta H = D_{C\text{-}H}$$

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V.2. Electronegativities

The original qualitative definition of Pauling is: " Electronegativity is the power of an atom in a molecule to attract electrons to it self."

It is not, however, the same as electron affinty, as will be seen. Suppose we consider a bond A-B between dissimilar atoms A and B. From The viewpoint of V.B. theory this will be a resonance hybrid

$$A—B \quad \leftrightarrow \quad A^- B^+ \quad \leftrightarrow \quad A^+ B^-$$

(a) (b) (c)

Pauling established a scale of electronegativities based on " excess " bond energies. The energynof the bond, D(A-B), is the sum of a nonpolar contribution, D_{np} (A-B), and a polar contribution, D_p (A-B). The nonpolar contribution is the energy expected from the mean of the nonpolar bond energies D(A-A) and D(B-B). The polar contribution, designated Δ, is a measure of the bond's expected polarity which results from a displacement of the electronic charge toward one atom. Ordinarily, the polarty of the bond increases with increasing differences in electronegativities of A and B.

$$D(A - B) = D_{np}(A - B) + \Delta_p(A - B)$$

$$D_{np}(A - B) = \frac{D_{np}(A \square A) \square D_{np}(b \square B)}{2}$$

$$D_r(A - B) = \Delta = D(A - B) - \frac{D_{np}(A \square A) \square D_{np}(B \square B)}{2}$$

The negative values can be avoided by using the geometric mean of the bond energies ($\sqrt{D(A \square A) \square D(B \square B)}$) to give Δ' values.

$$\Delta' = D(A - B) - \sqrt{D(A \square A) \square D(B \square B)}$$

Note that in each case D(A - B) is greater than the geometric mean of D(A - A) and D(B -B). This mean energy is taken as the (hypothetical) A - B bond energy if the A - B bond were purely covalent, that is, represented only by canonical form (a). The differences, Δ's, are identified as "ionic resonance energies" due to resonance of (a) with (b). It is assumed that the greater the

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electronegativity difference the more ionic resonance there will be, and hence the larger will be the value of Δ. However, Δ is not proportional to the electronegativity differences $x_A - x_B$. Thus

$$(x_F - x_{Si}) - (x_{Br} - x_{Si}) = (x_F - x_{Br})$$

but $$89 - 25 \neq 16$$

In general the quantities $\Delta^{1/2}$ do seen to be additive or approximately so. In the present case

$$9.3 - 5.0 = 4.3 \approx 4.0$$

Pauling set up a table of relative electronegativityes using the relation

$$x_A - x_B = K \times \Delta^{1/2}$$

The constant K was taken as $23^{-1/2}$ (Δ's were expresed in eV). Amoung the dozens of other methods proposed for estimating experimentally or calculating electronegativity values, we shall mention only two.

Mulliken showed by theoretical arguments that the tendency of an atom in a molecule to complete with another atom to which it is bound in attracting the shared electrons should be proportional to (J + A) /2, that is to overage of its ionization potential and its electron affinity. It is found that when J an A values are expressed in electron volts the hulliken electronegativity values can be adjusted to give the least mean deviation from Pauling's by dividing then by 3.15.

The empirical method of Allred and Rochow seems to have certain advantages stemming precisely from its complete and strict empiricism. An electron in a bond is assumed to be attracted by one of two nuclei according to Coulomb's law.

$$\text{Force} = \frac{Z^{\square} e^2}{r^2}$$

where Z^* is the effective nuclear charge which the electron feels and r is its mean distance from the nucleus.

Z^* is estimated using the Slater's method, and r is taken as the covalent radius of the atom, which for a homonuclear diatomic molecule is half the internuclear distance.

Equation Allred and Rochow's electronegativities is obtained:

$$x_{AR} = 0.359 \frac{Z^{\square}}{r^2} \square 0.744$$

The electronegativity of an element is dependent of its valence (i.e. for S in SCl_2 has a different electronegativity from S in SF_6).

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V. 3. Bond Lengths and Covalent Radii

The lengths of bonds, are the intermolecular distances in molecules. If we consider a homonuclear diatomic molecule with a single bond; such as F_2 or Cl_2, we can assign to the atoms F and Cl covalent single bond radii equal to one-half of the internuclear distances in the respective molecules.

The covalent radius of the chlorine atom is one half of the chlorine-chlorine distance. The elements which form molecules with many bonds other methods of estimating the radii are used. For example, the triple bond radii of carbon and nitrogen can be calculated for the bond lengths in HC≡CH and N≡N, as 0.60 and 0.55, giving 1.15 for –C≡N as compared to experimental values of ≈ 1.16. The higher the order of a bond between two atoms, the shorter it is (i.e. C–C 1.54; C=C 1.33; C≡C 1.21).

The C–C distance in diamond is found to be 1.54 ± 0.01 A°, so the covalent radius of C is taken as 1.54/2 = 0.77.

In the molecules where there are bonds between atoms of disparate electronegativities the bond length can be calculated by the Schomaker-Stevenson equation

$$r_{A-B} = r_A + r_B - 0.09 | x_A - x_B |$$

This relationship is not very satisfactory because in some molecules there are posibilities of double bonding. For example in the case of BF_3 the bond shortening can also be attributed to B–F double bonding since boron has a vacant p_z orbital and the fluorine atoms have a filled p_z orbitals.

It is probable that both ionic-covalent resonance and multiple bonding contribute significantly.

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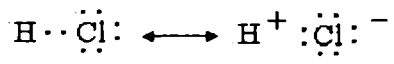
V. 4. Bond and Molecular Polarity

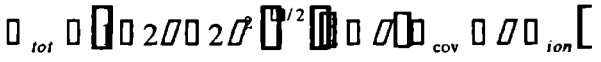
The electrical polarity of a molecule is expressed as its dipole moment. A system consisting of a positive charge, + x, and a negative charge, - x, separated by a distance, d, possesses a dipole moment of a magnitude xd. If x is equal to the electronic charge (4.80×10^{-10} e.s.u) and d is 1^{oo} A°, xd = 4.80 D (Debye) units. The dipole moment is a vector quantity since it has a definite direction as well as magnitude.

The electronic structure of Hcl can be expressed in a very simple way by writing it as an ionic-covalent resonance hybrid of two Lewis structures:



(a) (b)

we may use equation for the total wave function of MO:



and define the percent ionic character as 100 λ. The internuclear distance in Hcl is 1.27 A°. If λ were unity, the dipole moment would be 6.1 D.

$$\mu = x \times d = 1.27 \times 4.80 = 6.1 \text{ D}$$

μ represents the expected dipole moment for 100% ionic HCl. The percentage of ionic character is obtained from the ratio of the observed dipole moment to the dipole moment for complete electron transfer.

The observed dipole moment for HCl is 1.03 D (1.03/6.1 - 17% i.e., λ = 0.17).

By plotting the various percentages obtained against $x_X - x_H$, where x_X is the electronegativity of the halogen atom, he obtained a smooth curve given by the equation

$$i\% = 18(x_X - x_H)^{1.4}$$

The main source of error is the assumption that Ψ_{cov} is nonpolar.

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V. 4.1. Polar nature of a heteronuclear bond

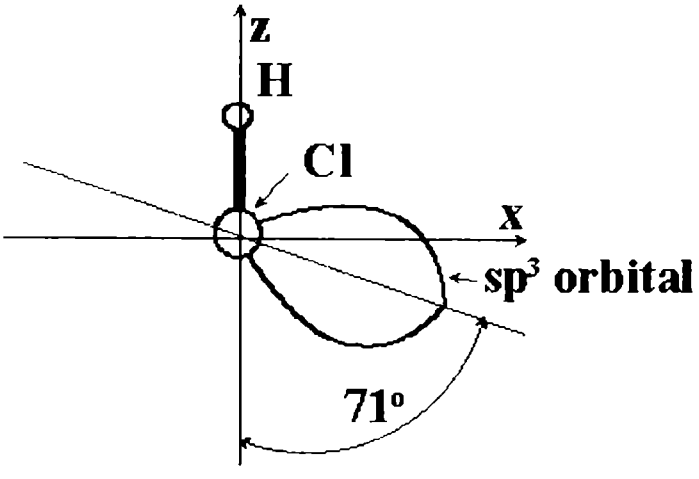
The Hcl molecule is a neutral system. If we place the centroid of charge of these two bonding electrons exactly half way between the nuclei, the system will have no dipole moment. However, since the hydrogen orbital is much smaller than the chlorine orbital, thecentroid of charge for the bonding electrons must be closer to H than to Cl and a dipole will result, namely,

$$\overleftarrow{H - Cl}.$$

V. 4.2. Orbital moments of unshared electrons

In the HCl molecule the chlorine atom has three pairs of electrons which have a orbital dipole moment vector of magnitude V pointing along the axis of the orbital. If the three pairs of electrons lie in the three equivalent hybrid orbitals, and the bond direction lie on the Z axis, the total dipole moment contribution in the bond direction is - 3V cos 71°, namely,

$$\overrightarrow{-3V\cos 71^{0}}$$
$$H - Cl$$



The dipole moment of a polyatomic molecule can be considered to be the vector sum of various contributing dipols. Suppose we have a regular pyramidal molecule, AB_3. Because of its symmetry its dipole moment must lie along the three-fold axis of symmetry. If each A-B bond axis makes an angle, θ, with this symmetry axis, we might say the net molecular dipole moment, μ, is the vector sum of three equal bond moments, each of magnitude $(\mu/3)\cos\theta$.

Unfortunately, this picture is unsatisfactory. The dipole moments of the pyramidal molecules NH_3 and NF_3 of 1.5 and 0.2 D respectively can not be explained only if we consider the influences to the dipole moment both of the bond moments and orbital moments of unshared pairs

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of electrons. In Figure 32 we shown the dipole moments of NH_3 and NF_3.

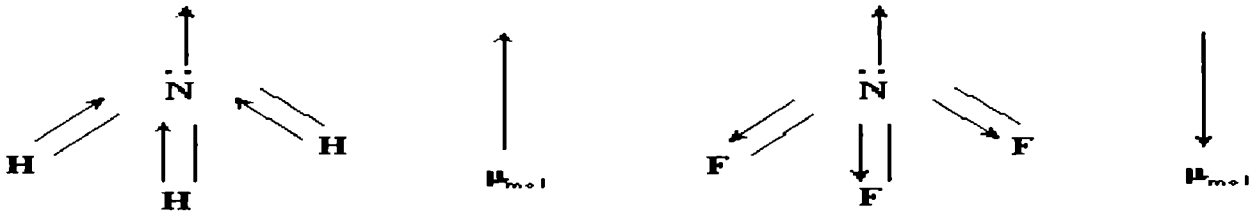

Figure 32 - Diagram illustrating how the molecular dipole moment, μ_{mol}, can be regarded as a vector sum, of bond moments and the lone pair moment in NH_3 and NF_3

It is possible that the orbitals are not directed exactly along the internuclear lines. That is, the bonds may be a little bent.

V. 5. Some Relations between Bond Properties

A bond property whose magnitude is directly related to the bond order is the force constant of the bond. The force constant of a bond between atoms A and B is given by equation.

$$\nu(cm^{-1}) = \frac{1}{c}\sqrt{\frac{f}{4\pi^2\mu}}$$

ν is the vibration frequency of the bond expressed in wave numbers (cm^{-1}), observed in IR or Raman spectrum

c is velocity of light

μ is the reduced mass of the A-B oscillator in grams

Specifically, we have the following relationships.

(1) As bond order increases:

length decreases

energy increases

force constant increases

(2) As bond length increases:

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energy decreases

force constant decreases

(3) As energy increases:

length decreases

force constant increases

(4) As force constant increases:

length decreases

energy increases

None of these relations is linear.

Repulsive force is proportional to $\frac{1}{l^{10\text{–}12}}$,

l is the bond length.

V. 6. Coordinative Covalence or Dative Bonding

Carbon monoxide provides a common case of molecule formation in which an s electron of carbon is not promoted. Here we would expect carbon to have achieved the configuration and oxygen to have an $s^2 p^6$ configuration.

However, the high dissociation energy of CO and the very short C-O bond distance suggest that the Lewis structure is better represented by

$$^{(-)}:C \equiv O:^{(+)} \text{ or simply } :C \equiv O:$$

The arrow in the right-hand formula is a convention sometimes used to indicate that oxygen donated both of the electrons in the bond. This so-called coordinate covalent bond, or dative bond cannot be distinguished from an ordinary covalent bond once it is formed.

The charges shown, called formal charges, and these may be calculated by assining half of the electrons shared between two atoms to each atom and calculating the resulting charge on the quasi ion.

The sum of the formal charges in a molecule will be zero.

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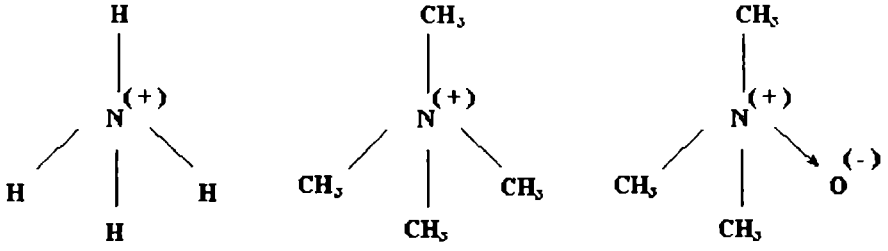
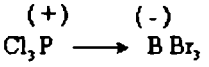
Formal charges are assigned assuming 100% covalent character, whereas oxidation number assignments assume no electron sharing.

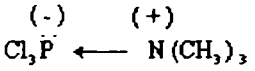
Nitrogen can form dative bonds as follows.



An arrow may be used for the N→ O bond, since it can be identified as the dative bond. Arrow are not appropriate for NH_4^+ or $N^+(CH_3)_4$, because the four bonds are equivalent. Phosphorus can donate its unshared pair in dative bonding, as in



or it can accept a pair of electrons into ad orbital as in

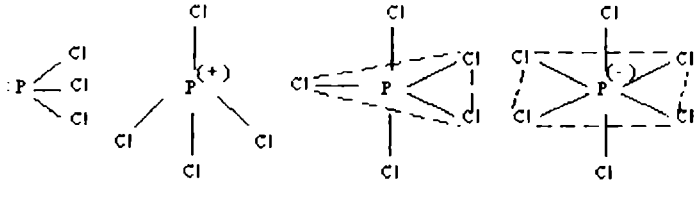


Phosphorus in PF_5 can add a fluoride ion by accepting a pair of electrons into one of its empty **d** orbitals, as shown below.

Electron configuration of PF_5

Electron configuration of PF_6^-

Through dive bonding, phosphorus can form four and six bonds, as well as the usual compounds such as PX_3 and PX_5. This series may be illustrated by the following species.



In addition to the compounds XX', XX'_3, XX'_5, XX'_7 for the heavier halogens, dative bonding allows the formation of ICl_2^-, ICl_4^-, and IF_6^-. Halogens can also form two bridging bonds, as shown in Figure 33.

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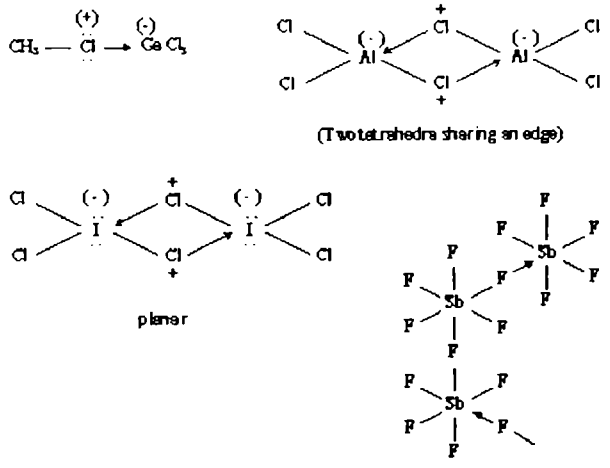
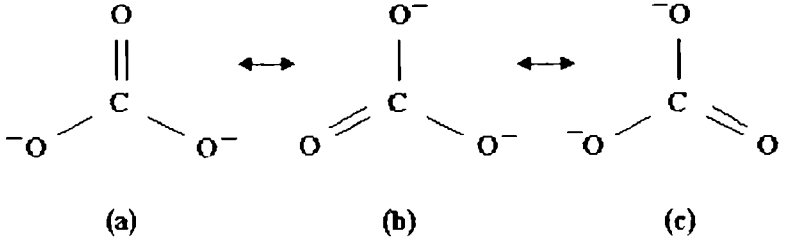


V. 7. Resonance

Some molecules or ions cannot be represented adequately by a single valence bond formula. Pauling introduced the concept of resonance to adopt the simple valence bond notation to situations in which electrons are delocalized. Three structures are written for the carbonate:



Do not interpret the three contributing structures as having any independent existence. There isn't an equilibrium among the three structures. The assignment of a bond order of 1 1/3 to the C–O bond in carbonates is straight forward, since the three most resonable contributing structures are equivalent. For example, the sulfate ion, may be viewed as arising from dative bonding between a sulfide ion and four oxygen atoms (a), or from the sharing of two pairs of electrons between each oxygen are sulfur (b). In addition to these extenes, we may write the intermediate structures (c); The actual structure of the sulfate ion would be are overage of all the structures shown, weighted according to the number of equivalent structures and their relative

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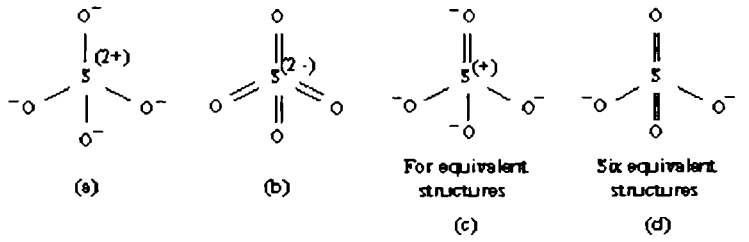
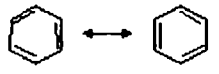
It has been estimated that the bond order in sulfates is approximately 1.5, corresponding most closely to (d).



The familiar application of resonance to benzene includes, the usual Kekulé structures (a and b)



The elimination of unlikely structures and the selection of the more important contributing structures, is facilitated by the following rules.

1. The contributing structures should have the same or nearly the same atomic positions. The closer the bond angles and the lengths of a contributing structure are to those of the actual molecule, the greater the " contributions " of that structure to the hybrid.

(c) and (d) are less important

2. All contributing structures of a particular molecule must have the same number of un paired electrons.
3. Contributing structures should not differ too widely in the positions of electrons or not differ greatly in energy. This rule also eliminates structures in which there are more than eight electrons around an atom.
4. Like charges should not reside on atoms close together in a contributing structure. In NH_3, structure (c) is relatively un important, because of the (+) charges on adjacent N atoms and also because of the double negative charge on the remaining N atom.

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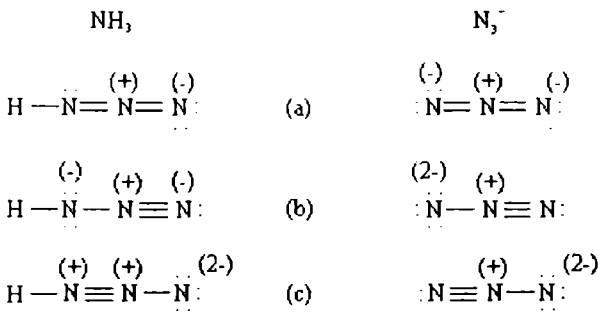

Since the similar structure for the N_3^- ion does not give (+) charges on adjacent N atoms, it should be more important than for the molecular acid. The change in the relative importance of the last contributing structure should result in the same bond order (about 2) for each bond in N_3^-, but in a bond order less than 2 for the N– N bond nearer the H atom and a bond order greater than 2 for the terminal N– N bond in HN_3. In N_3^- there is a resonance stabilization of the anion.

5. Contributing structures in which negative charge resides on an electronegative element and positive charge resides on an electropositive element are more important than those in which the reserve is true. For HF the contributing structure $H^{(+)}$ $F^{(-)}$ is an important one: the ionic structure $H^{(+)}$ $F^{(-)}$is not.
6. The greater the number of covalent bonds, the greater the importance of a contributing structure. In the case of pyridine-N-oxide, structures (c-e) have a favorable distribution of charges from the standpoint of the electronegativity of the atoms involved, but the fact that these structures contain one less bond than the (a and b) structures diminishes their importance.

Rule 5 indicates that structures (f-h) should be even less important than (a) and (b), because the (+) charge is on the more electronegative nitrogen and the (-) charge is on a carbon atom.

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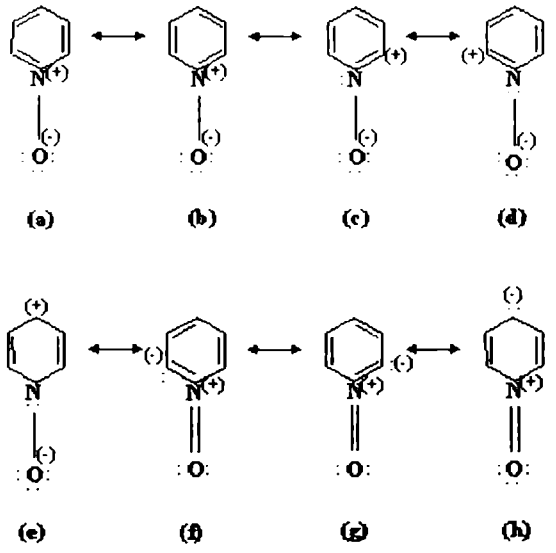

The discrepancy between calculated and observed heats of formation is called the resonance energy. Typical resonance energies (KJ/mole) are benyene, 155; naphthalene, 314; C≡O, 439; and O=C=O, 151; The increased stability of molecules stabilized by resonance is reflected in the shortening of bond lengths compared to the overage expected from the contributing structures.

The greater the number of contributing structure the greater the delocalization of electronic charge and hence the more stable the molecular delocalization of charge on an atom is usually an unstable situation. The increasing acidity in the series HCl O, $HClO_2$, $HClO_3$,

---

$HClO_4$ is determined largely by the greater stability of the anions containing several oxygen

---

atoms, because of the greater delocalization of the negative charge. For the most part, the

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negative charge in ClO^- must reside on the oxygen atom. In ClO_4^- the negative charge is spread over four equivalent oxygen atoms

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V.8. Gases, liquids, solids

V.8.1. Gases

V.8.1.1. Introduction

At O level you would have learnt that matter can exist in three physical states - solid, liquid and gas. This is summarised in Fig. 8.1.

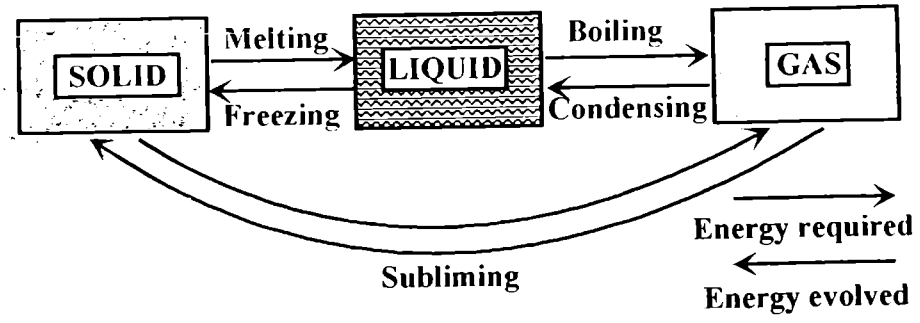

Figure 8.1 - States of matter and their interconversion

A more detailed study of these three states of matter will be required at A level. It is important to remember that gases, liquids and solids are readily interconverted by changes of temperature and pressure.

There are various gas laws that you need to know. Some of these you will have met at O level, or possibly in O level or A level physics. Many of these laws only apply to **ideal gases**. Gases are never strictly ideal and it is necessary to understand why and how these laws can be applied to the non-ideal situation.

One difficulty that you might encounter with subject is the difference in units of pressure used. Looking at A level papers in recent years you will see:

(i) Pascal (Pa). This can be written as Nm^{-2} (newtons per square metre) or kg m^{-1} sec^{-2} Standard pressure corresponds to 101 325 Pa or 101.325 kPa. (100 kPa is sometimes called 1 bar and so standard pressure is approximately 1 bar.)

(ii) Millimetres of mercury (mm Hg). This is height of a mercury column in mimmimetres supported by that pressure. Standard pressure corresponds to 760 mm Hg.

(iii) Atmosphere (atm). This is useful for measuring high pressures. Standard pressure is 1 atmosphere.

The important thing to remember is that unless the question asks for specific units it does not matter to you or the examiner which units you use providing you use your units consistently.

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V.8.1.1.2. Gas laws

Changes in temperature and pressure have little effect on the volume of a liquid or a solid, but a considerable effect on the volume of a gas. Various gas laws have been devised following experiments and they are considered individually in Units 8.3. - 8.7.

V.8.1.1.3. Boyle's law

The volume of a fixed mass of gas is inversely proportional to pressure providing the temperature is kept constant.

i.e. as the pressure ***P*** increases, the volume ***V*** decreases. This is expressed mathematically as

$$P \propto \text{constant} \times \frac{1}{V}$$

A graph of ***P*** against **1/*V*** is a straight line passing through the origin.

V.8.1.4. Charles' law

The volume of a fixed mass of gas, at constant pressure, is directly proportional to the absolute temperature.

i.e. as the pressure ***P*** increases and the particles move faster, they move farther apart and the volume ***V*** increases.

Mathematically, V = constant × T, where T is temperature in degrees K (The temperature in degrees Kelvin (K) is found by adding 273° to the temperature Celsius *e.g.* 20°C = 20 + 273 = 293K).

This law is based upon work done by Gay Lussac. He found that a gas expands or contracts by approximately 1/273 of its volume at 0°C for every °C that the temperature rises or falls.

273 cm^3 of gas at 0°C will have a volume of 272 cm^3 at -1°C, 263 cm^3 at -10°C, and 293 cm^3 at 20°C. If the gas were cooled to -273°C (0 K) its volume would theoretically be zero. -273°C (0 K) is called the **absolute zero** and is the starting point of the Kelvin scale.

Boyle's law and Carles'law can be combined in a general gas equation.

$$\frac{p_1V_1}{T_1} \propto \frac{p_2V_2}{T_2}$$

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This equation is useful for correcting the volume of a fixed mass of gas under one set of conditions of temperature and pressure to the volume of gas under a different set of conditions.

If a gas is at 0°C (273 K) and 101.3 kPa, these conditions are called **standard temperature and pressure** (stp).

Example: A fixed mass of gas has a volume of 76 cm^3 at 27°C and 100 kPa pressure. Find the volume that the gas would have at stp.

V_1 = volume before correction = 76 cm^3
P_1 = pressure before correction = 100 kPa
T_1 = temperature before correction = 300 K

V_2 = volume after correction - unknown
P_2 = pressure after correction = 101.3 kPa
T_2 = temperature after correction = 273 K

Substitute in $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$$\frac{100 \times 76}{300} = \frac{101.3}{273} \times V_2$$

$$V_2 = 68.3 \text{ cm}^3$$

Since both the pressure has increased and the temperature has decreased, it is expected that the answer would be less than 76 cm^3.

V.8.1.5. Ideal gas equation

This equation applies only for ideal gases. The equation is

$$PV = nRT$$

where P = pressure, V = volume, n = number of moles of gas, R = molar gas constant and T = absolute temperature.

The **molar gas constant** R is the same for all gases. It can be calculated using the information that 1 mole of a gas at 0°C and 101 325 Pa pressure occupies 0.0224 m^3.

Substituting in the equation $PV = nRT$

$$R = \frac{101325 \times 0.0224}{1 \times 273} = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

The value for R is given on the examination paper and it is important that the units you use are in agreement with the units for R.

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V.8.1.6. Dalton's law of partial pressure

In a mixture of gases, the total pressure is equal to the sum of the partial pressures of the individual gases.

Mathematically, for three gases A, B and C in a mixture,

$$P = P_A + P_B + P_C$$

where P is the total pressure of the mixture, P_A is the partial pressure of A, P_B is the partial pressure of B, P_C is the partial pressure of C.

The **partial pressure** of a gas is the pressure that the gas would exert if it alone occupied the whole volume of the mixture at the same temperature. For A the partial pressure

$$P_A = \frac{\text{number of moles of A} \times \text{total pressure}}{\text{total number of moles in mixture}}$$

Example: Calculate the partial pressures of carbon dioxide and oxygen in a mixture of the two gases with total pressure 100 kPa. The mixture consists of 4.4g of carbon dioxide and 6.4g of oxygen (Relative atomic masses C =12, O = 16)

$$\text{Number of moles of carbon dioxide} = \frac{\text{mass of carbon dioxide}}{\text{relative molecular mass of carbon dioxide}}$$

$$\frac{4.4}{12 + 2 \times 16} = 0.1 \text{ moles}$$

$$\text{Number of moles of oxygen molecules} = \frac{\text{mass of oxygen}}{\text{relative molecular mass of oxygen}}$$

$$\frac{6.4}{32} = 0.2 \text{ moles}$$

Total number of moles of carbon dioxide and oxygen = 0.1 + 0.2 = 0.3 mole.

$$\text{Partial pressure of carbon dioxide} = \frac{\text{no. of moles } CO_2 \times \text{total pressure}}{\text{total number of moles}}$$

$$\frac{0.1}{0.3} \times 100 \text{ kPa} = 33.3 \text{ kPa}$$

$$\text{Partial pressure of oxygen} = \frac{\text{no. of moles oxygen} \times \text{total pressure}}{\text{total number of moles}}$$

$$\frac{0.2}{0.3} \times 100 \text{ kPa} = 66.6 \text{ kPa}$$

(Check that the two answers add up to the total pressure)

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V.8.1.7. Avogadro's hypothesis and Gay Lussac's law

Avogadro's hypothesis states that equal volumes of different gases under the same conditions of temperature and pressure, contain the same number of molecules.

Gay lussac's law states that the volumes of gases reacting and the volumes of products if gaseous bear a simple numerical relation to one another, providing all measurements are made at the same temperature and pressure.

For example, by experiment, it can be found that 10 cm^3 of nitrogen gas (1 volume) combines with 30 cm^3 of hydrogen gas (3 volumes) to produce 20 cm^3 of ammonia gas (2 volumes).

Find the volume of oxygen required and the volume of gaseous product formed when 10 cm^3 of methane CH_4 is burnt in sufficient oxygen for complete combustion.

All measurements were made at room temperature and pressure.

First write the equation.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\text{methane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

$$1\ \text{vol} \qquad 2\ \text{vol} \qquad 1\ \text{vol} \qquad 0$$

When 10 cm^3 of methane gas (CH_4) reacts, 20 cm^3 of oxygen is required.

Volume of carbon dioxide produced = 10 cm^3.

(NB When gases are cooled to room temperature, the steam condenses and the volume of water produced is negligible)

V.8.1.8. Vapour density

The vapour density of a gas or vapour is given by

$$\text{vapour density} = \frac{\text{mass of a volume of the gas}}{\text{mass of an equal volume of hydrogen}}$$

at the same pressure and temperature.

Since equals volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules (Avogadro's hypothesis)

$$\text{vapour density} = \frac{\text{mass of } n \text{ molecules of gas}}{\text{mass of } n \text{ molecules of hydrogen}}$$

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$$\square \frac{\text{mass of 1 molecule of gas}}{\text{mass of 1 molecule of hydrogen}}$$

But relative molecular mass = $\frac{\text{mass of 1 molecule of gas}}{\text{mass of 1 atom of hydrogen}}$

Since a molecule of hydrogen is composed of 2 atoms

Relative molecular mass = 2 × vapour density

The relative molecular mass of a gas or volatile liquid can be finding the vapour density of the vapour produced.

V.8.1.9 Graham's law of diffusion

The rate of diffusion of a gas is inversely proportional to the square root of its density (d).

$$\text{rate of diffusion} \propto \sqrt{\frac{1}{d}}$$

If two gases diffuse under the same conditions of temperature and pressure, then

$$\frac{\text{rate of diffusion of gas 1}}{\text{rate of diffusion of gas2}} \square \sqrt{\frac{\text{mass of 1 mole of molecules of gas2}}{\text{mass of 1 mole of molecules of gas 1}}}$$

Example: In an experiment 100 cm^3 of methane (CH_4 , relative molecular mass 16) diffuses in 24 seconds. Under the same conditions of temperature and pressure, 200 cm^3 of sulphur dioxide diffuse in 96 seconds. What is the mass of 1 mole of molecules of sulphur dioxide?

Rate of diffusion of methane = $\frac{100}{24}$ $cm^3\ s^{-1}$

rate of diffusion of sulphur dioxide = $\frac{200}{96}$ $cm^3\ s^{-1}$

Substituting in the above equation

$\frac{100/24}{200/96} \square \sqrt{\frac{M}{16}}$ where M is the mass of 1 mole of molecules of sulphur dioxide $M = 64$

V.8.1.10. The kinetic theory of gases

In a gas, the particles of the gas are in continual rapid, random motion. The particles are very widely spaced. The pressure of a gas is the result of continuous collisions between the particles and the walls of the container.

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The following assumptions are made for ideal gases:

(i) The particles are in a state of continuous random motion.

(ii) The volume of the particles is negligible compared to the total volume of the gas.

(iii) The attractive forces between the particles are negligible.

(iv) The collision between particles of the gas are perfectly elastic - no energy is exchanged when the particles collide.

V.8.1.11. Real and non ideal gases

The ideal gas does not exist in practice; two of the major assumptions of an ideal gas are that its particles are negligible in volume and the forces of attraction between the molecules are negligible.

A gas behaves more ideally at low pressure (when the molecules are widely spaced) and high temperature (when molecules are moving rapidly and the intermolecular forces are not significant). In other words when the gas is under conditions most like a gas and least like a liquid.

The gas laws and the ideal gas equation relate only to ideal gases. The ideal gas equation is modified in van der Waals' equation.

$\left(P + \frac{a}{V^2}\right)(V - b) = n R T$ where a and b are constants for a particular gas.

The term $\left(P + \frac{a}{V^2}\right)$ takes account of the intermolecular forces in the gas and the term *(V - b)* compensates for the volume of the particles in the gas.

The forces which exist between the molecules in a gas are mostly due to van der Waals' forces, dipole-dipole attraction or hydrogen bonding.

V.8.1.12. Velocities of the molecules in a gas

At a particular temperature, the molecules in a gas moving with a wide range of velocities (and a wide range of kinetic enegies). Only a relatively few molecules possess low or high velocities. Fig.V.4 shows the distribution of velocities of the molecules in a gas. An increase in temperature causes a shift towards higher velocities and a flattening of the peak indicates that a wider range of velocities exist.

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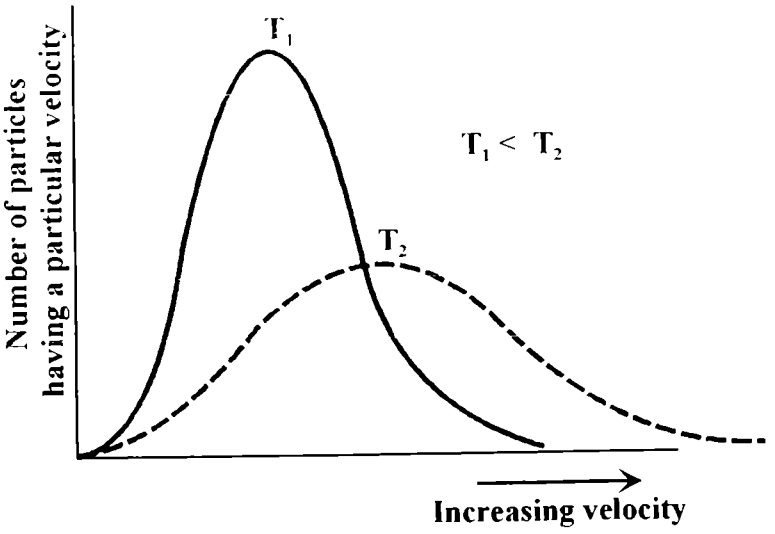

Figure V.4 – Distribution of velocities of molecules in a gas

V.8.2. Liquids

V.8.2.1. Liquefying gases

A gas may be liquefied by cooling the gas or increasing the pressure (within limits discussed below). Andrews (1861) carried out experiments to investigate the effect of changes of temperature and pressure on the volume of carbon dioxide. The results are summarised in Figure V.5

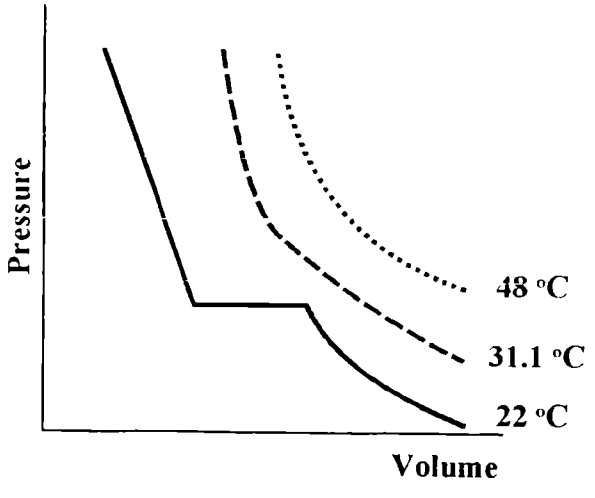

Figure V.5 - Andrews' isothermals

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Each curve represents the variation of volume of a fixed mass of carbon dioxide with changes of pressure and at constant temperature. These curves are called **isothermals**. The isothermals at 48°C represents the usual behavior of a gas. The isothermal at 22°C shows a horizontal portion where the volume changes rapidly for only a small change in pressure. This horizontal portion corresponds to liquefaction of carbon dioxide. Ther is only a slight kink in the isothermal at 31.1°C. At this temperature liquefaction barely occurs and at temperatures higher than this liquefaction can not be achieved by simply increasing pressure. This temperature is called the **critical temperature** of carbon dioxide. The critical temperature is that temperature above which a gas cannot be liquefied by applying pressure. The minimum pressure required to liquefy a gas at its critical temperature is called the **critical pressure**.

V.8.2.2. The liquid state

The particles in a liquid are much closer together than the particles in a gas. They are constantly moving and colliding. This is illustrated by **Brownian motion**. Particles of pollen on the surface of water are in a state of constant random motion. This movement of pollen grains can be seen with a microscope and can be explained by the constant bombardament of the pollen grains by water molecules.

The particles are moving with different kinetic energies. Some of the particles possess greater than average kinetic energy and, close to the surface of the liquid, may ascape from the liquid into the space above. This process is called **evaporation** and, because the particles have above average kinetic energies, the temperature of the liquid falls during evaporation.

V.8.2.3. Vapour pressure

Consider a liquid in a cloused container with a vacuum in the space above the liquid. The system is kept at constant temperature. Molecules of the liquid escape from the liquid into the space above the liquid. Eventually, an equilibrium is produced. Molecules are still leaving the liquid, but molecules are also hitting the surface of the liquid and are re-entering the liquid. In this equilibrium the pressure in the space above the liquid is unchanged and is called the **satured vapour pressure** of the liquid at that temperature.

At a higher temperature, the molecules in the liquid possess greater kinetic energies and more escape. The gaseous molecules are moving faster and more collide with the surface and re-

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enter. An equilibrium is again set up but there are more molecules in the space and, therefore, the vapour pressure is greater.

V.8.2.4. Phase diagrams for one-component systems

A **phase** is defined as a part of the whole system which is physically distinct from the rest of the system but its composition is the same throughout (i.e. it is homogenous). A mixture of gases or a solution are examples of a single phase.

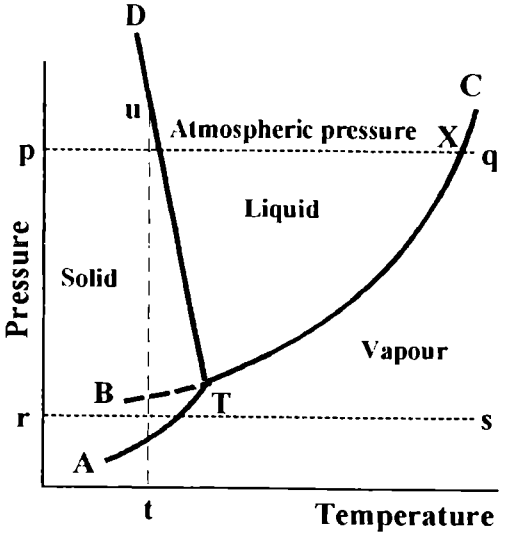

Figure V.6 - Phase diagram for water

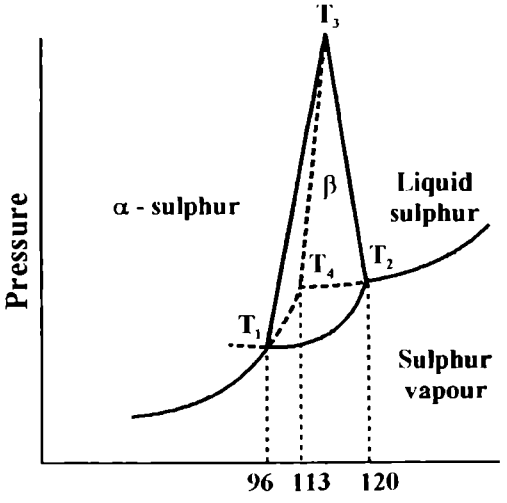

Figure V.7 - Phase diagram for sulphur

V.6 shows a phase diagram for water. It is a diagram showing how the physical state of water changes with changes in temperature and pressure.

Refering to Fig. V.6, TC represents the change of vapour pressure of liquid water with temperature. The line pq represents atmospheric pressure. TC meets pq at X. X is the boiling point of water.

TD represents the equilibrium between solid and liquid i.e. the change of melting point of ice with change in pressure. As the pressure increases, the melting point of ice decreases but big changes in pressure are required to make a significant change in melting point. For all substances apart from water, antimony and bismuth, the line DT slopes slightly forward (rather than slightly backward) and an increase in pressure produces a slight increase in the melting point.

AT represents the equilibrium between solid and vapour and TB represents the **supercooling** of liquid water.

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Point T iscalled the **triple point** and under this set of conditions ice, water and water vapour can be in equilibrium together. For water, this unique situation exists at 0.0075°C and 530Pa pressure.

Point C is called the **critical point**. Above this pressure (22.12 x 10^3kPa) and this temperature (647.4 K) a gas cannot be liquefied by decreasing only the temperature or increasing only the pressure.

If a sample of ice is heated at atmospheric pressure, it changes from solid to liquid to vapour (follow dotted line pq). If a sample of ice is heated at a low pressure, the solid ice can turn directly to a vapour. Also under these conditions a vapour can turn directly to a solid (follow dotted line rs). This process is called **sublimation**.

A sample of water vapour maintained at constant temperature undergoes changes of state with increasing pressure. As the pressure increases, the water vapour turns directly to a solid and then at a higher pressure, the solid melts (follow dotted line tu).

A simple phase diagram has to be modified for substances which can exit in different forms in the same physical state. Sulphur, for example, shows enantiotropy and the phase diagram is shown in Fig. V.7.

Up to 96°C, α-sulphur is the stablle allotrope of solid sulphur. At the triple point T_1, α-sulphur, β-sulphur and sulphur vapour can exit in equilibrium. T_2 and T_3 are other triple points and T_4 is an unstable triple point point for α- sulphur, liquid sulphur and sulphur vapour.

V.8.3. Solids

V.8.3.1. Introduction

The particles in a solid may be atoms, ions or molecules In a solid, the particles are regularly arranged in a lattice and this regular arrangement causes the solid to be crystalline.

One of the difficulties with answering questions on the solid state is to represent, in two dimensions, crystal lattices which exit in three dimensions. It is important to practise drawing the diagrams in ths Unit.

In a lattice at OK, the particles would be stationy but at any temperature above they are vibrating. As the temperature is raised the particles vibrate even more about their positions in the lattice. When the lattice vibrations reach a certain level, the forces between the particles in the

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lattice are inadequate and the lattice breaks up. This process is called **melting**. At the melting point there is a dynamic equilibrium between particles in the solid state and particles in the liquid state.

V.8.3.2. X-ray diffraction

X-ray duffraction is used to determine the arrangements of particles in a solid. The wavelength of X-rays is approximately the same as the distance between the particles in the lattice (10^{-10}m).

X-rays are produced when cathode eays fall upon metals. A beam of X-rays (of the same wavelength) strikes a crystal and the X-rays are diffracted by the crystal and are detected by a photographic plate.

If a beam of X-rays strikes a crystal (Fig. V.8) with the waves of the X-rays in phase, the reflected eays will only remain in phase if the difference in distance travelled is a whole number of wavelengths.

If the X-rays are to remain in phase, then extra distance travelled=CB and BD and CB+BD = $n\lambda$ where n is an integer and λ is the wave length of the X-rays.

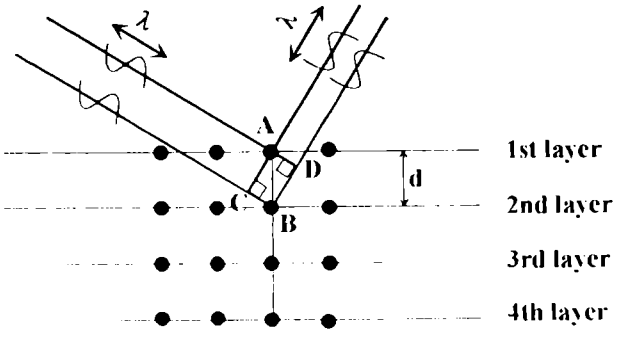

Fig. V.8 Beam of X-rays striking a crystal

If the angle between the crystal face and the incident X-ray is θ, then CAB and BAD equal θ By trigonometry, CB=AB sinθ and BD=AB sinθ. The distance AB is the distance between the first and second layers of particles in the crystal = d $\therefore 2d\sin\theta = n\lambda$

This equation is called the **Bragg equation**.

In a particular experiment, using one face of a crystal, the wavelength (λ) and the distance between the layers (d) is fixed. For a given angle θ , series of spots will appear on the photographic plate corresponding to n = 1, 2, 3 etc. From these results d can be calculated.

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X-ray diffeaction is used for a fine powder. Electron diffraction can also be used to determine the structure of a solid. Electrons, however, have a poorer penetrating power than X-rays.

V.8.3.3. Metal Crystal Structures

A metal consists of a close-paked regular arrangement of positive ions, which are surrounded by a'sea' of delocalosed electrons that bind the ions together. The ions in a close-packed layer are arranged in a regular hexagon.

The close-packed layers of ions can be stacked in two ways-both being equally likely. Some metals have one type of staking, some metals have the other type and some metals can exist in either depending upon the conditions. The two ways od stacking these layers are:

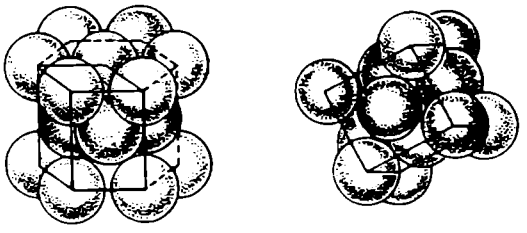

Figure V.9 - Hexagonal close packing (a) and cubic close packing (b)

(i) ABAB or **hexagonal close packing** (Fig. V.9*a*). The ions in the third layer are immediately above ions in the first layer. The stacking of the layers will continue ABAB... Magnesium and zinc are examples of metals with this structure.

(ii) ABC or **cubic close packing** (sometimes called face centred cubic) (Fig. V.9*b*). The ions in the third layer are not immedialely above ions in the first layer. The stacking of the layers will continue ABCABC... Aluminium and copper are examples of metals with this structure.

The difference between these two structures may be seen clearly in Fig V.10. The ions in the first layer are shown in continous lines. The ions in the second layer are shown in dotted lines. There are two sets of hollows in the second layer in which ions in the third layer can rest. These are labelled H or C. Ions cannot rest in both H and C. If they rest in hollows H, hexagonal close packing is produced but if they rest in hollows C, cubic close packing results.

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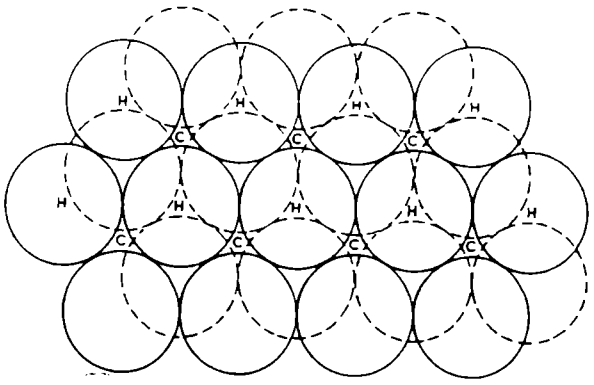
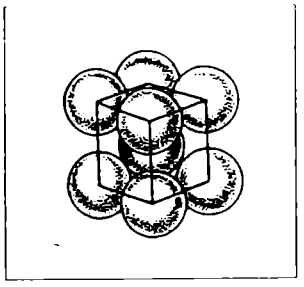


Figure V.10 - Difference between hexagonal close packing and cubic close packing

Figure V.11 - Body centred cubic structure



In both hexagonal close packing and cubic close packing any ion in the structure has twelve other ions touching it - six in the same layer, three in the layer above and three in the layer below. The number of ions in contact with any ion in the structure is called the **coordination number**. he coordination number in both close-packed structures is twelve. In both structures about 75% of the available space is filled by the ions.

Alkali metals and same other metals have a **body centred cubic** structure (Fig V.11). In this structure the ions are not as closely packed (about 32% of the available space is unfilled) This explains the low density of alkali metals. The coordination number in this structure is eight.

V.8.3.4. Ionic Crystals

An ionic crystal is a regular arrangement of positive and negative ions. The ions are held together by strong electrostatic forces. The sodium chloride lattice is shown in Fig. V.12. The sodium chloride lattice consists of a face centred cube of sodium ions and an inter-penetrating face centred cube of chloride ions.

In simple terms, each sodium ion in the lattice is surrounded by six chloride ions and each chloride ion by six sodium ions. The coordination is called 6:6.

Although sodium chloride NaCl and caesium chloride CsCl have similar formulae they have different crystal structures. In the caesium chloride structure (Fig. V.13), the coordination is 8:8. Eight chloride ions surround each caesium ion and eight caesium ions around each chloride ion.

The caesium ion is much larger than sodium ion (ionic radii Cs^+ 0.167 nm and Na^+ 0.098 nm). In sodium chloride, six chloride ions (ionic radius 0.181 nm) surround the sodium ion but, in

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caesium chloride, it is possible to pack eight chloride ions around each caesium atom.

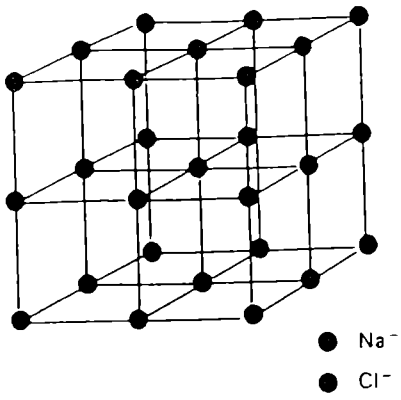


Figure V.12 - Structure of sodium chloride

Other substances with stoichiometry **XY** can have a similar structure to sodium chloride if the ratio of ionic radii is similar to

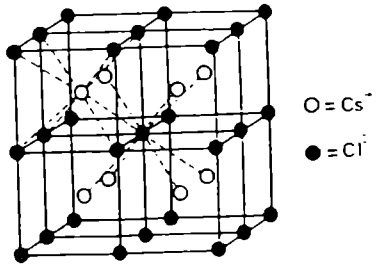
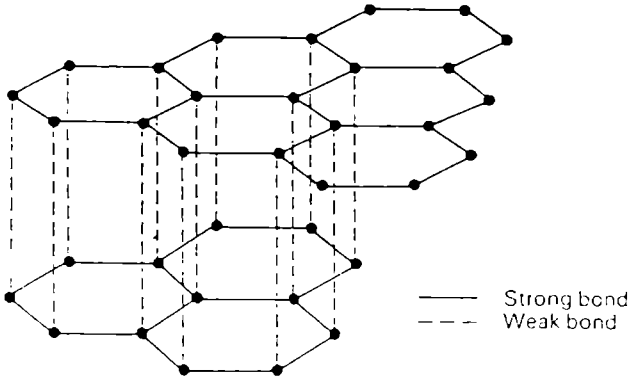


Figure V.13 - Structure of caesium chloride

the ratio in
sodium chloride.

V.8.3.5. Covalent Crystals



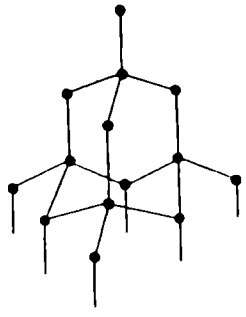


Figure V.14 - Structure of diamont

Crystals containing covalent bonding can be subdivided into:

(i) Giant covalent structures

In a giant covalent structure, the atoms are bonded together to give a three-dimensional (or two-dimensional) structure with a high melting point.

Diamond and graphite are two allotropic forms of carbon.

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In diamond (Fig. V.14) all of the carbon atoms are sp^3 hybridised and joined by fout covalent bonds to four other atoms towards the corners of a regular tetrahedron. All of the C–C bond lengths are the same. The bonds are very strong.

Graphite (Fig. V.15) is a layer structure. The carbon atoms in each layer are sp^2 hybridised and the bonds between carbon atoms in the layer are strong. The forces between the layers are weak Van der Waals'forces and the layers are able to slide over one another.

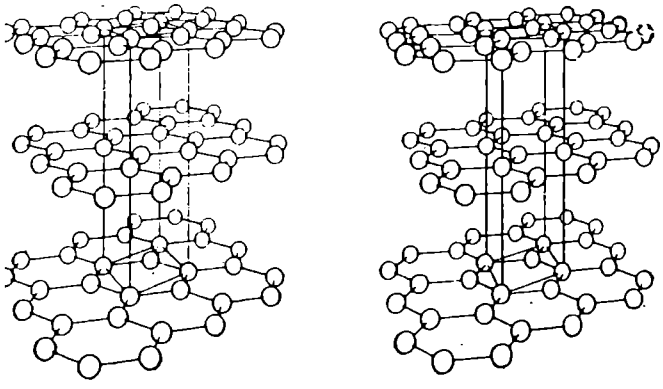

Figure V.15 - Structure of graphite

(ii) Molecular crystals

In a molecular crystal there are discrete molecules containing **strong** covalent bonds held together by **weak** Van der Waals' forces or hydrogen bonding. A substance which exists as molecular crystals melts at a low temperature because the weak forces are easily broken. Examples of molecular crystals are iodine and ice.

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VI SOLUTIONS

VI.1. Introduction

Most of the solution you have met in an O level course were solutions of solids in liquids. In this unit solutions of gases in liquids, liquids in liquids and solids on solids will be considered. This unit is closely linked with Unit 12 which deals with the colligative properties produced when a solute dissolves in a solvent.

A solutions is still a single phase but there are now or more components.

VI.2 Solutions of gases in liquid

Most gases dissolve in a solvent with the evolution of heat, *i.e.* the process is **exothermic**. In accordance with Le Chatelier's Principle, the solubility is decreased by increasing temperature.

The most important factor affecting the solubility of a gas in a solvent is expressed by **Henry's law**: the mass of gas dissolved by a given volume of solvent, to give a saturated solution, is directly proportional to the pressure of the gas, providing the temperature remains constant and there is no reaction between the gas and the solvent.

Gases such as ammonia, hydrogen chloride and carbon dioxide react when they are dissolved in water. The law does not apply to these gases but applies satisfactorily for gases such as oxygen, hydrogen, helium etc.

The solubility of a gas in a liquid is usually expressed as an **absorption coefficient**. This is defined as the number of cm^3 of gas at stp which saturate 1 cm^3 of the liquid at a given temperature and 1 atm (10.3kPa).

If a mixture of gases is in equilibrium with a solvent (*e.g.* air with water) each gas dissolves according to its own partial pressure.

VI.3 Solutions of liquids in liquids

In this section it is useful to consider the mixing of two completely miscible ideal liquids and then to consider the effects of deviations from ideality. Ideal liquids show no heat or volume change when they are mixed and obey Raoult's Law over the whole composition range.

Raoult's Law states that the vapour pressure of a constituent of an ideal solution is

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equal to the vapour pressure exerted by the pure constituent at that temperature multiplied by the mole fraction of that constituent.

Mole fraction is a convenient way of expressing the composition of each component in a mixture. The mole fraction of A in a mixture A and B

$$X_A = \frac{n_A}{n_A + n_B}$$

The mole fraction of B

$$X_B = \frac{n_B}{n_A + n_B}$$

The sum of the mole fractions of the components in the mixture equals one.

$$n_A + n_B = 1$$

Raoult's Law can be expressed as

$$P_A = X_A P_A^o$$

where: P_A is the vapour pressure of A over the liquid

X_A is the mole fraction of A

P^o_A is the vapour pressure of A over pure A at that temperature.

Similarly

$$P_B = X_B P_B^o$$

Total pressure of vapour over the liquid $P = P_A + P_B$. This is expressed in the graph in Figure VI.1

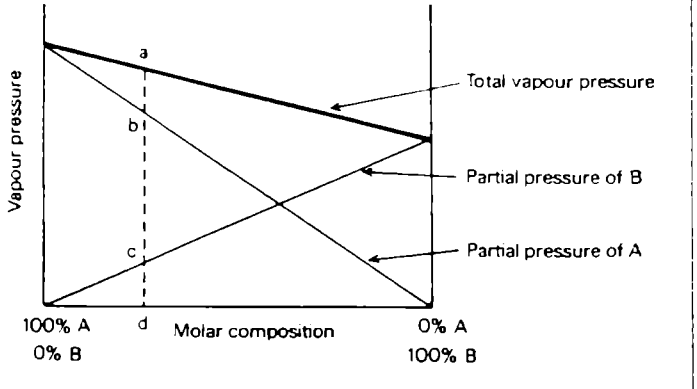

Figure VI.1 Pressure of vapour over a liquid for a mixture of A and B

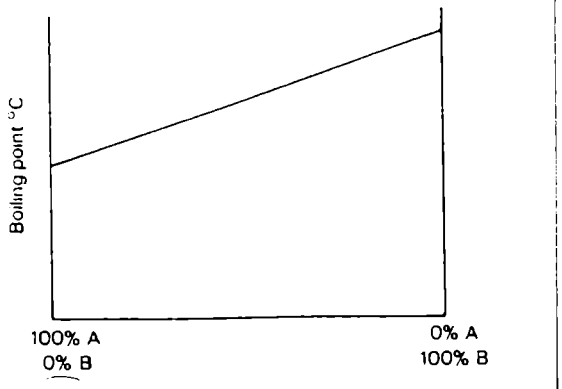

Figure VI.2 Boiling point/composition curves for a mixture of A

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The vertical dotted line represents a solution of composition 20% B and 80% A. The total vapour pressure of this solution ad is equal to the sum of the partial pressure due to A (db) and the partial pressure due to B (cd).

Figure 11.2 shows the boiling point/composition curve for the same mixture of A and B. A liquid which has a high vapour pressure will have a low boiling point and *vice versa*.

Some pairs of liquids obey Raoult's Law closely *e.g.* benzene and methylbenzene or hexane and heptane. The two components in each mixture are very similar chemically. Figure 11.3 shows the vapour boiling

point diagrams for a mixture of hexane and heptane.

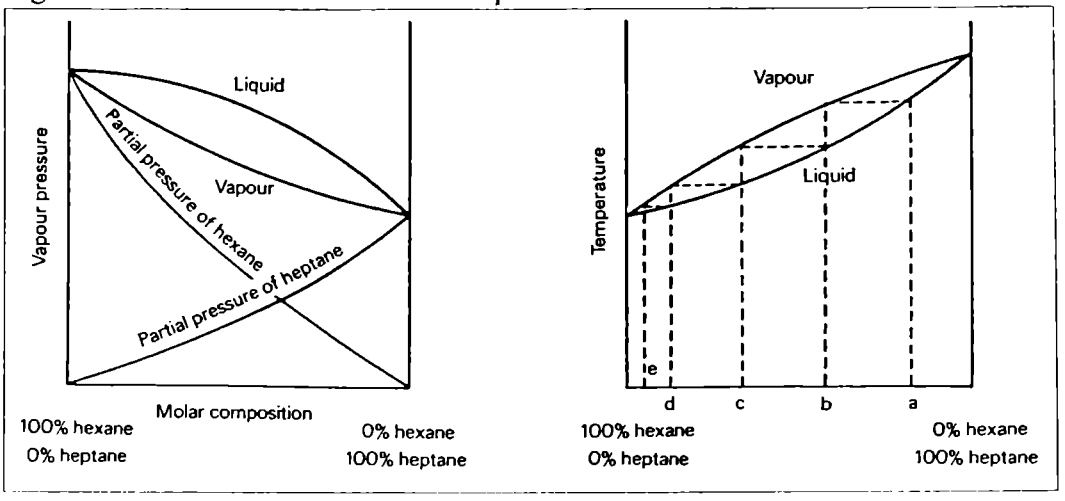

Figure VI.3 - Vapour pressure and boiling point diagrams for a mixture of hexane and heptane

The biggest difference between the vapour pressure/composition curve in Figure 11.3 and the ideal curve in Figure 11.1 is the existence of separate curves for the composition of the liquid and vapour.

In the temperature/composition curve, the variation of the boiling point of the liquid with composition of the liquid is shown by the curve labelled 'liquid'. The 'vapour' curve shows the composition of the vapour in equilibrium with a liquid mixture at its boiling point. The composition of the vapour in equilibrium with a liquid of any composition is always richer in the more volatile (lower boiling point) component.

When a mixture of hexane and heptane of composition *a* (Fig.11.3 *b*) is heated, the vapour which is in equilibrium with this mixture has a composition *b* (richer in hexane). If this vapour is condensed the liquid still has the composition *b*. If this liquid is reheated the liquid of composition

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b is in equilibrium with the vapour of composition *c*. Each step produces a liquid richer in the lower boiling point component. Further repetition of this process will eventually give pure hexane.

Rather than carry out in a series of steps, it is usual to carry it out in one stage using a **fractionating column**. A series of condensations and evaporations take place as the vapour moves up the column. Fractional distillation is used to separate the components of a pair of miscible liquids that are near ideal.

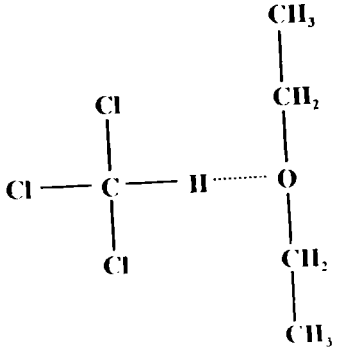
VI.4. Deviation from Raoult's law

Deviations from ideal behavior can be of two types - positive and negative deviations.

Negative deviations

If trichloromethane ethoxyethane are mexed together the temperature rises. This is because extra

intermolecular forces exist in the mixture which do not exist in the pure liquids.



These extra. weak hydrogen bonds **reduce** the vapour pressure of the mixture of liquids and **increase** the boiling point. On the vapour pressure/composition graph there is a minimum, and on the temperature/composition graph a maximum (Fig.11.4).

A mixture of ethoxyethane and trichloromethane of composition **X** distils over without change of composition and with boiling point **T**. A mixture of this type is called an **azeotropic** or **constant boiling point** mixture.

If a mixture of any other composition is heated, one of the pure components ethoxyethane and trichloromethane distils off until the composition of mixture becomes the same as the

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azeotropic mixture. Then the pure azeotropic mixture distils off. Whether ethoxyethane or trichloromethane distils off first depends upon which one is in excess. Other examples of pairs of liquids behaving in this way include: hydrochloric acid and water, and sulphuric acid and water.

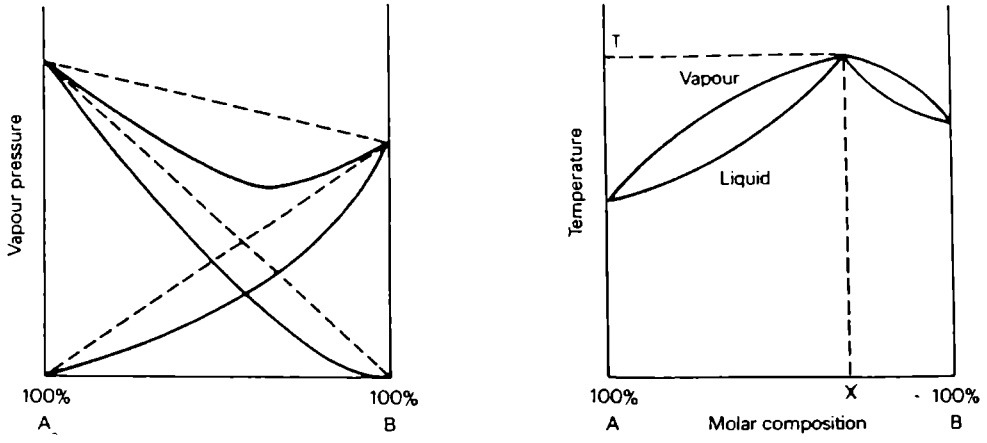


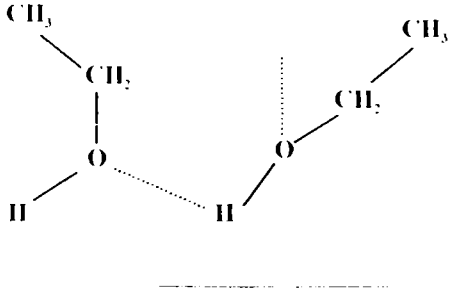
Figure VI.4 - Vapour pressure/composition and temperature/composition graphs (minimum vapour pressure)

Positive deviations

When trichloromethane and ethanol are mixed together the temperature falls. There are strong forces of hydrogen bonding which exist in pure ethanol.

When the liquids are mixed, the hydrogen bonds are broken. The tendency for molecules to escape, therefore, increases. This **increases** the vapour pressure and **reduces** the boiling point- there is a minimum on the temperature/composition graph (Fig.VI.5).

The mixture of composition **X** distils over without change of composition. Fractional distillation of a mixture will produce the azeotropic mixture **X** and this will distil over until one of the components is



used up. The remaining component distils over pure.

A mixture of ethanol and water behaves in this way. When a mixture of 10% ethanol and 90% water is heated, the azeotropic mixture containing 95.6% ethanol and 4.4% water distils over

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until all the ethanol has been used up. Then pure water distils over. it is impossible to obtain pure ethanol by distilling solutions of ethanol in water.

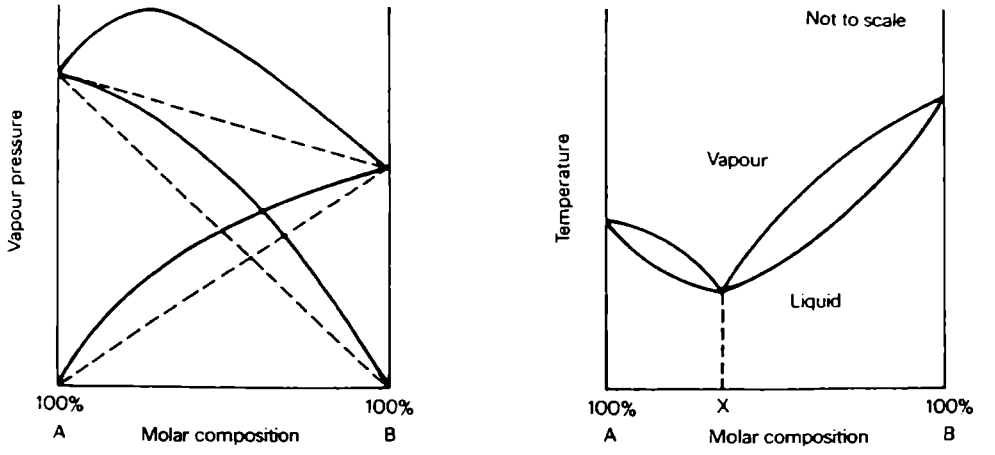

Figure 11.5 - Vapour pressure/composition and temperature/composition graphs (maximum vapour pressure)

VI.5 Volumetric calculations

VI.5.1. Introduction

Volumetric calculations are required for theory papers and often on practical papers. These calculations involve reactions between reacting volumes of solutions. When attempting this type of question it is important to ensure that you have a balanced equation for the reaction.

e.g. $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

From the equation, 2 moles of sodium hydroxide react with 1 mole of sulphuric acid. If 25 cm^3 of sodium hydroxide solution (0.1 mol dm^{-3}, although this may still be shown as 0.1 molar of 0.1M) is neutralised by 20 cm^3 of sulphuric acid, we can use this equation to find the concentration of the sulphuric acid in mol dm^{-3}.

Sodium hydroxide

1000 cm^3 of sodium hydroxide (0.1 mol dm^{-3}) contain 0.1 moles of of sodium hydroxide.

25 cm^3 of 0.1 mol dm^{-3} sodium hydroxide contains $\frac{0.1 \times 25}{1000}$ moles = 0.0025 moles

From the equation,

2 moles of sodium hydroxide react with 1 mole of sulphuric acid

0.0025 moles NaOH react with 0.00125 moles H_2SO_4

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0.00125 moles of sulphuric acid are present in 20 cm^3 of solution.

$\frac{0.00125 \times 1000}{20}$ moles of sulphuric acid would be present in 1000 cm^3.

Molar concentration of sulphuric acid = 0.0625 mol dm^{-3}

All calculation can be worked out in a similar way. The method of working is far better than simply substituting in the equation

$$n_2V_1M_1 = n_1V_2M_2$$

where n_1 = number of moles of sulphuric acid in the equation = 1

V_1 = volume of sulphuric acid used = 20 cm^3

M_1 = molar concentration of sulphuric acid - unknown

n_2 = no. of moles of sodium hydroxide in the equation = 2

V_2 = volume of sodium hydroxide solution used = 25 cm^3

M_2 = molar concentration of sodium hydroxide = 0.1 mol dm^{-3}

If you substitute the figures in the equation you will get correct answer, but the problem comes when you make a mistake. The examiner has difficulty in awarding marks if you make a mistake in substituting in an equation. In the first method of calculation, marks can be awarded at each stage if an error is made.

VI.5.2. Types of volumetric calculation

There are three types of volumetric analysis questions which appear on theory papers.

1 Acid - base titration

The one above between sodium hydroxide and sulphuric acid in example.

2 Redox titrations

These can be of two types but in both cases they involve transfer of electrons

(i) Reactions involving acidified potassium manganate(VII) or potassium dichromate(VI).

(ii) The reactions of iodine solution with sodium thiosulphate(VI). In some cases the iodine for titration is liberated from acidified potassium iodide solution by an oxidising agent such as potassium manganate(VII), potassium iodate(V) or copper(II) sulphate.

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3 Precipitation titrations

The usual example here is the reaction of silver nitrate solution with chloride ions to precipitate silver chloride. The end point is usually detected with potassium chromate(VI) solution as indicator.

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VII. COLLIGATIVE PROPERTIES

VII.1. Introduction

When a non-volatile solute is added to a solvent, there are changes in certain colligative properties. A **colligative property** is a property which depends upon the number of particles in a given volume of solvent and not the nature of the particles. Colligative property measurements are used to determine the relative molecular masses of dissolved solutes.

The four colligative properties are:

(i) lowering of vapour pressure;

(ii) elevation of boiling point;

(iii) depression of freezing point;

(iv) osmotic pressure.

Each of these four properties will be considered separately. It is important to remember that the determination of relative molecular masses can be carried out only if non-electrolytes are used in dilute solution.

VII.2. Lowering of vapour pressure

If a non-volatile solute, *e.g.* urea, is added to water, there is a lowering of vapour pressure of the solution.

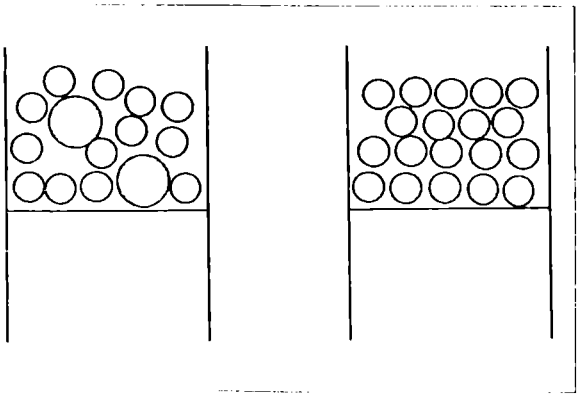

Figure VII.1 - Vapour pressure of solutions

In Figure VII.1*a*, all of the pure solvent molecules at the surface can escape into the vapour if they possess sufficient energy. In the dilute solution *(b)* the solid circles represent solute molecules which are involatile hence there are a reduced number of molecules at that temperature which can escape into the vapour and, therefore, a lowering of vapour pressure.

There is a relationship between the lowering of vapour pressure and the concentration of solution. It is given by Raoult's law.

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Raoult's Law states that the relative lowering of vapour pressure is equal to the mole fraction of the solute.

$$\frac{P^o - P}{P^o} = \frac{n}{N + n}$$

where P^o represents the vapour pressure of the pure solvent, P represents the vapour pressure of the solution, n is the number of moles of solute and N is the number of moles of solvent.

If the masses of solvent and solute are W and w respectively and the relative molecular masses of solvent and solute are M and m, the equation becomes:

$$\frac{P^o - P}{P^o} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

For very dilute solutions, the number of moles of solute is small and the above expression approximates to:

$$\frac{P^o - P}{P^o} = \frac{n}{N}$$

One problem that a candidate has is to decide whether to use the approximation or work out the answer in full. The best advice is to work out the answer without using the approximation. With a calculator it does not take much longer. Use the approximate expression if you have insufficient time or if the question asks for an approximate answer.

Raoult's law applies only to dilute solutions.

Example: 10g of a non-volatile solute **X** were dissolved in 90g of water. The vapour pressure of this solution was lowered to 742 mm. The vapou pressure of water at this temperature was 750 mm. Calculate the relative molecular mass of solute **X**.

Substitute in the above equation, knowing that the relative molecular mass of water is 18.

$$\frac{750 - 742}{750} = \frac{\frac{10}{M}}{\frac{10}{M} + \frac{90}{18}} = 186$$

(If you had used the approximation, you would have obtained a value of 187).

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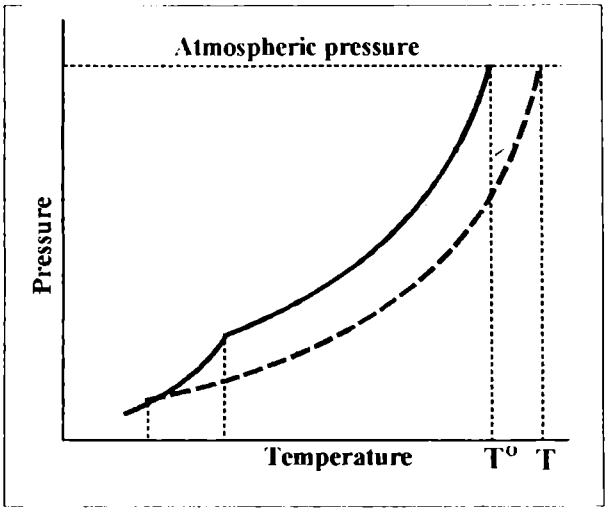
VII 3. Elevation of boiling point

Figure VII.2 shows - the dotted curve represents the vapour pressure of the dilute solution and the solid line the vapour pressure of the pure solvent. The vapour pressure of the solution is less than the vapour pressure of the pure solvent at all temperatures. In consequence, the vapour pressure of the dilute solution does not reach atmospheric pressure until a higher temperature.

For dilute solutions, the elevation of boiling point $(T - T^{o})$ is proportional to the lowering of the vapour pressure.

Figure VII.2 - Elevation of boiling point



$$\Delta T \alpha P^{o} - P$$

$$\Delta T \quad k (P^{o} - P) \qquad (1)$$

Raoult's law for very dilute solutions is:

$$\frac{P^{o} \square P}{P^{o}} \square \frac{n}{N} \qquad (P^{o} \square P) \square \frac{P^{o} n}{N}$$

Substituting in equation (1)

$$\square T \square k P^{o} \frac{n}{N}$$

The vapour pressure of a solvent is constant at a particular temperature. Therefore, kP^{o} is a constant.

$$\text{Now, } n \square \frac{w}{m} \text{ and } N \square \frac{W}{M}$$

$$\square T \square k' \frac{w M}{m W}$$

If a fixed mass of 1000g of solvent is taken, the ratio $\frac{M}{W}$ is a constant.

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$$\Delta T = \frac{Kw}{m}$$

where K is called the boiling point (or ebulliscopic) constant,

w is the mass of solute

m is the **relative molecular mass** of the solute.

The boiling point constant is the elevation of boiling point which would occur if one mole of a non-ionising and non-volatile solute is dissolved in 1000g of solvent.

The experimental determination of the relative molecular mass of urea in solution in water can be carried out by elevation of boiling point measurements. Using the apparatus in Figure 12.3, steam is passed

through the water in the graduated tube until the water starts to boil. The temperature of the boiling water is recorded.

A weighed amount of solute is dissolved in the water in the graduated tube and steam is again passed until the solution boils. The temperature of the solution and the final volume of the solution are recorded. Heating the solution with steam prevents superheating.

Example: Calculate the relative molecular mass of a non volatile solute from the following results:

1.00g of solute dissolved in 40g of benzene causes the boiling point to be elevated by 0.20°C. The boiling point constant for benzene is 2.7°C kg^{-1}.

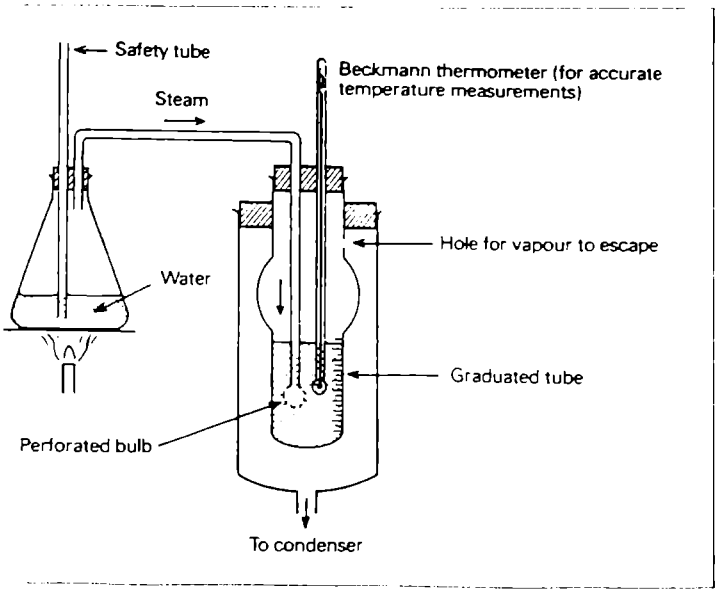

Figure VII.3 - Apparatus to determine elevation of boiling point

The equation $\Delta T = \frac{Kw}{m}$ can be used where ΔT = 0.20°C, K = 2.7°C kg^{-1}, w = mass of solute in 1000g benzene = 25g

$$m = \frac{2.7 \times 25}{0.2} = 337.5$$

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The problem with using an equation is that if you get the equation incorrect you are unlikely to pick up any marks.

An alternative method, starting from first principles, is:

1 mole (*i.e.* mg) of solute dissolved in 100g of solvent elevates boiling point by 2.7°C.

1g of solute dissolved in 1000g of solvent elevates boiling point by $\frac{2.7^\circ C}{m}$

(elevation of boiling point $\propto$ concentration)

1g of solute dissolved in 40g of solvent elevates boiling point by $\frac{2.7}{m} \times \frac{1000}{40}$

(This solution is more concentrated and therefore elevation of boiling point is greater).

$$\frac{2.7}{m} \times \frac{1000}{40} = 0.2 \quad ; m = 337.5$$

VII.4. Depression of freezing point

A dilute solution freezes at a slightly lower temperature than the pure solvent. This small difference in temperature is called the **depression of freezing point**.

For dilute solutions, the depression of freezing point is proportional to the lowering of vapour pressure. The equation

$$\Delta T \propto K \frac{w}{m}$$

applies but in this case K is called the **freezing** point(or cryoscopic) constant. It is the depression of freezing point which would occur if one mole of any non-ionising and non-volatile solute were dissolved in 1000g of solvent. The depression of freezing point can be found using the apparatus in Figure 12.4.

A known mass of the solvent is put into the centre tube and stirred thoroughly to minimise supercooling. The temperature is recorded every half minute and a cooling curve is plotted.

The solvent is then warmed until it melts and a known mass of solute is added to the solvent. The cooling process is repeated and the new freezing point is determined.

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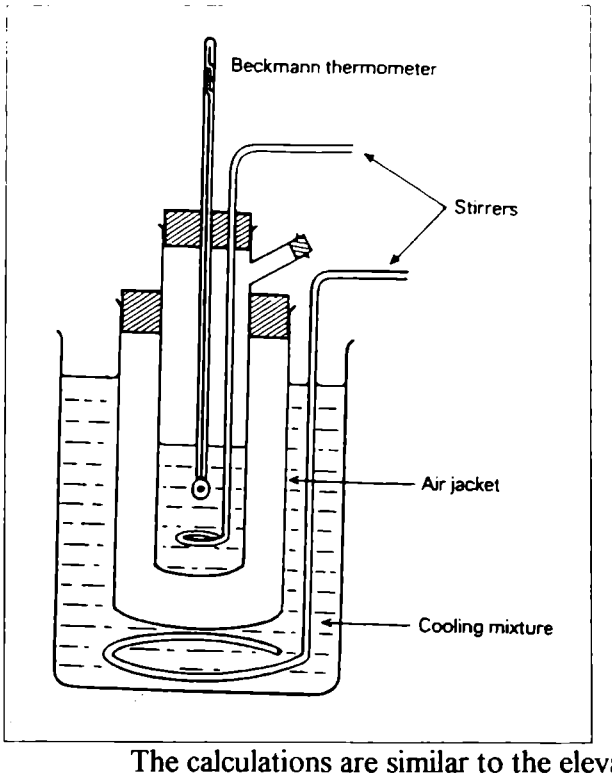

Figure VII.4 - Apparatus to determine depression of freezing point

The calculations are similar to the elevation of boiling point calculations.

VII.5. Osmosis and asmotic pressure

If two solutions of different concentrations are separated by a semi-permeable membrane, solvent molecules pass through the membrane and equalise the concentrations of the two solutions. This process is called **osmosis**. Solvent molecules pass through the membrane in both directions but the rate at which the solvent passes from the dilute to the concentrated solutions is greater than the reverse rate.

A semi-permeable membrane is a membrane which will allow solvent molecules but not solute molecules to pass through it. The simplest semi-permeable membrane is a piece of pig's bladder but this is not very strong in practice. A good semi-permeable membrane is produced when copper(II) hexacyanoferrate(II) is precipitated in a porous pot.

The apparatus in Figure 12.5 is used to demonstrate osmosis.

Over a period of time the water level in the tube rises as the water molecules pass through the semi-permeable membrane into the sugar solution.

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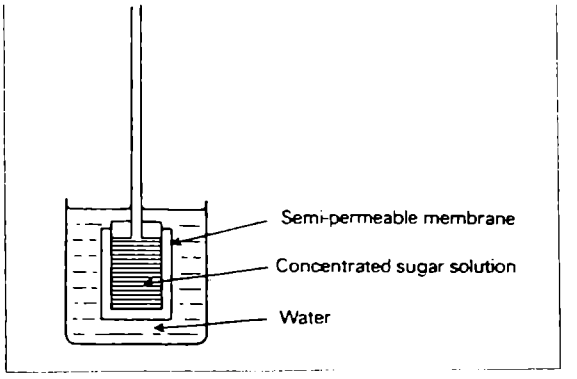
Figure VII.5 - Apparatus to demonstrate osmosis



When the level in the tube no longer rises, the pressure of this column of solution is equal to the **osmotic pressure**. The osmotic pressure of a solution is the pressure which has to be applied to the solution side of a semi-permeable membrane in order *just* to prevent passage of solvent molecules from pure solvent on the other side of the membrane into the solution. Solutions which have the same osmotic pressure are said to be **isotonic**.

The two laws of osmosis are:

(i) At a given temperature, the osmotic pressure Π (pi) of a dilute solution is proportional to the concentration **c**.

$$\mathrm{P} \propto \mathbf{c} \text{ (but } \mathbf{c} \propto \frac{1}{V} \therefore \Pi \propto \frac{1}{V})$$

(ii) The osmotic pressure of a given solution is directly proportional to the absolute temperature $\Pi \propto \mathrm{T}$.

These two laws are similar to Boyle's and Charles' laws for gases. They can be combined to form an equation.

$\Pi V = nRT$ where the value of R is equal to the gas constant. The number of moles of solute $n = \frac{w}{m}$ where w = mass of solute and m is the relative molecular mass of the solute.

$$m = \frac{wRT}{\Pi V}$$

Osmotic pressure measurements can be used to find the relative molecular mass of a non-ionised solute. It is particularly useful for polymers which produce such small elevations of boiling point or depressions of freezing point that relative molecular masses cannot be determined accurately by these methods.

VII.6. Abnormal relative molecular masses

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Accurate relative molecular masses can be obtained for undissociated solutes in dilute solution. For partially or completely dissociated solutes the relative molecular masses obtained will be less than the true value due to the extra particles present.

For partially dissociated electrolyte AB, the following equilibrium exists:

$$AB \leftrightarrow A^{+} + B$$

If one mole of AB is used and a moles of AB have dissociated, after dissociation

$(1 - \alpha)$	α	α
moles	moles	moles

The ratio of the number of particles after dissociation and before dissociation is $\frac{1+\alpha}{1}$

This is equal to the van't Hoff factor i where

$$i = \frac{\text{observed effect on colligative property}}{\text{calculated effect on colligative property}}$$

By equating, the value of a can be calculated. It is important to realise that an electrolyte $CaCl_2$ does not dossociate as before.

$$CaCl_2 \leftrightarrow Ca^{2+} + 2Cl^{-}$$

	$1 - \alpha$	α	2α

$$\frac{\text{Number of moles after dissociation}}{\text{Number of moles before}} = \frac{1+2\alpha}{1}$$

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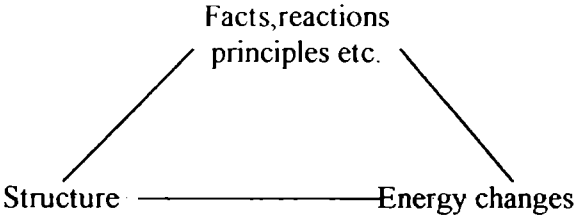
VIII. ENERGETICS

VIII.1. Introduction

At O level a study of chemistry can be summarised by the following triangle.



The emphasis at O level must be towards the learning of fact, principles, and reactions, with structure and energy changes being less important. The extent to which structure and energy changes are introduced varies from one syllabus to another.

For example, the melting of ice to give water is a simple process and a straightforward topic which O level candidates should know. As an A level candidate you should appreciate that ice has an open crystal lattice with a tetrahedral structure. On heating, the water molecules in the lattice vibrate more and the structure breaks up on melting. The process requires energy:

e.g. ice + energy → liquid water

This is an **endothermic** process and the energy required is called the **enthalpy change of fusion**.

You should always consider changes of structure and energy changes when answering questions. Nearly all chemical reactions involve energy changes and study of energy changes is called **energetics**.

VIII.2. First law of thermodynamics

This law is equivalent of the law of conservation of energy. It states that **energy cannot be created or destroyed but may be converted from one form into another**

$$q \quad \Delta U + w$$

where ΔU is the change in the internal energy

q is the actual heat change, and

w is the work done by the system.

The term w involves the gas produced expanding and pushing back the atmosphere. This can be estimated by using a syringe with a piston. The work done

$w \quad P\Delta V$ where P is external pressure and ΔV is the change in volume.

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$P\Delta V$ (and hence w) only becomes significant when either P and/or ΔV is large. In reactions involving only solids and liquids as reactants and products $P\Delta V$ is negligible. For gases ΔV is frequently large and w can be significant.

Reactions carried out at constant volume. In these cases $\Delta V = 0$ (*i.e.* no change in volume) and $P\Delta V \quad w \quad 0$

$$q_v \quad \Delta U$$

q_v represents heat change at constant volume. Any heat change recorded corresponds to a change in the internal energy of the system.

Reactions carried out at constant pressure. Most reactions carried out in the laboratory are carried out at constant pressure *e.g.* in an open beaker. Work is done by any gas expanding against the pressure of the atmosphere.

$q_v = \Delta U + P\Delta V$ where q_v represents the heat change at constant pressure

$$q_v = (U_{final} - U_{initial}) + P(V_{final} - V_{initial})$$

$$(U_{final} + PV_{final}) \; (U_{initial} + PV_{initial})$$

The term $U + PV$ represents the energy possessed by the system and is called the **enthalpy** or **heat content** H:

$$q_v = H_{final} - H_{initial} = \Delta H$$

Substituting,

$$\Delta H = \Delta U + P\Delta V$$

VIII.3. Enthalpy change of reaction

The equation for the reaction between carbon and excess oxygen is

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta H \quad -393.5 \text{ kJ mol}^{-1}$$

(Note mol^{-1} means per quantity shown in the equation *not* per mole of product.)

The combustion of 12g of graphite in excess oxygen liberates 393.5 kJ. (The negative sign for ΔH, by convention, tells us that energy is **liberated** or the reaction is **exothermic**).

The quantity of energy liberated or absorbed is given by the equation, ΔH is called the **enthalpy change of reaction**. Often standard enthalpy changes are quoted. These are the enthalpy changes at standard atmospheric pressure and at constant temperature, usually 25°C (or 298 K).

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The reactants and products are in their usual or standard states at 25°C. Carbon is in the form of graphite and oxygen and carbon dioxide are gases. The standard enthalpy change of reaction is represented by ΔH°. If solutions are used they must have a concentration of 1 mol dm^{-3}.

It is impossible to estimate absolute enthalpies but only enthalpy changes. Elements in their standard states are regarded as having zero enthalpy.

There are a number of standard enthalpy changes which are important and should be clearly defined.

VIII.4. Standard enthalpy change of formation

The standard enthalpy changes of formation of a compound is the energy given out or taken in when one mole of the compound is formed from its constituent elements in their standard states at 25°C.

For example, ΔH_f^0 = -393.5 kJ mol^{-1} for the formation of carbon dioxide.

VIII.5. Standard enthalpy change of combustion

The standard enthalpy changes of combustion of a subtance ΔH_c^0 is the enthalpy change when one mole of the substance in its standard state undergoes complete combustion.

If the compound contains carbon, hydrogen and oxygen, the complete combustion will produce carbon dioxide and water.

e.g. $C_2H_6(g) + 3\frac{1}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ ΔH_c^0 = -1560 kJ mol^{-1}.

In any chemical reaction the change of the enthalpy is:

$$aA + bB \rightarrow cC + dD$$

$$\Delta H \quad \Delta H_{products} - \Delta H_{reactants}$$

$$\Delta H \quad c\Delta H_C + d\Delta H_D - (a\Delta H_A + b\Delta H_B)$$

$$\Delta H \quad \Sigma n_p H_p - \Sigma n_r H_r$$

VIII.6. Standard enthalpy change of neutralization

The standard enthalpy change of neutralization is the enthalpy change when 1 mole of H3O+ ions is just neutralized by an alkali in dilute solution. The acid and base are in their standard states at 25°C and the acid and base are in solution containing 1 mol dm^{-3}.

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$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H_c^0 = -57.1$ kJ mol^{-1}

The values obtained for standard enthalpy changes of neutralization of strong acids and strong bases are constant.

VIII.7. Enthalpy change of solution and enthalpy change of dilution

The enthalpy change of solution is the enthalpy change when 1 mole of subtance is dissolved in a specified volume of solvent. The enthalpy change will depend upon the volume of solvent used.

The enthalpy change of dilution is the enthalpy change when 1 mole of subtance is dissolved in a large volume of solvent such that further dilution produces no further enthalpy change.

VIII.8. Measuring enthalpy change

Enthalpy change are determined by simple calorimetry experiments. For example to determine the enthalpy change of neutralization of sodium hydroxide and hydrochloric acid, a known volume of sodium hydroxide solution of known concentration is placed in a vacuum flask and the temperature is accurately measured. The volume of hydrochloric acid, of known concentration, required to neutralize the sodium hydroxide solution is rapidly added, the mixture stirred and the final temperature recorded.

If the initial temperature of both the acid and alkali is t_1°C and the final temperature is t_2°C, the temperature change is $t_2 - t_1$°C. If the mass of the mixture is mg, the specific heat capacity of the solution is 4.2 J deg^{-1} (dilute solutions can be assumed to have the same specific heat capacity as water), and the heat capacity of the vacuum flask is W, then

$$\text{heat evolved} = m \times 4.2 \times (t_2 - t_1) + W \times (t_2 - t_1) \text{ J}$$

From these results the enthalpy change of neutralization can be calculated.

VIII.9. Hess's law

Hess's law can be used for calculating enthalpy changes which cannot be determined by experiment. the law states that the total enthalpy change for a reaction is independent of the route taken.

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For example if X is converted to Y and Y to Z, the total enthalpy change will be the same as when X is converted directly to Z.

Exemple: Calculate the standard enthalpy change of formation of carbon monoxide from the following information:

Enthalpy changes of combustion of carbon (graphite) and carbon monoxide are -393.5 kJ mol^{-1} and -283 kJ mol^{-1}.

The following equation can be written

Required: Enthalpy change of formation of carbon monoxide

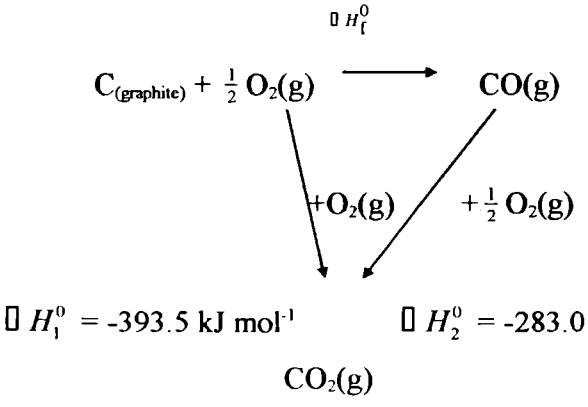
$$C(graphite) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$$

Given: Enthalpy change of combustion of graphite and carbon monoxide

(i) $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^o = -393.5$ kJ

(ii) $CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^o = -283$ kJ

A diagram can be draw to summarise the situation



$$\Delta H_1^0 = \Delta H_1^0 - \Delta H_1^0 = -393.5 + 283.0 = -110.5 \text{ kJ mol}^{-1}$$

Alternatively, from equation *(i)* and *(ii)* above, equation *(ii)* can b ereversed when the enthalpy change is the same numerically but the sign is changed.

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^o = -393.5$ kJ

$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2} O_2(g)$ $\quad \Delta H^o = +283$ kJ

Adding these two equations together

$C(graphite) + \tfrac{1}{2} O_2(g) \rightarrow CO(g)$ $\quad \Delta H_f^0 = -393.5 + 283.0 = -110.5$ kJ mol^{-1}

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The **negative** sign shows, by convention, that the process is **exothermic**. A **positive** sign shows that the process is **endothermic**. Candidate lose many marks in this type of work by either getting a sign wrong or by missing out units. It is advisable when an enthalpy change is positive to put in a positive sign. This shows the examiner that you have thought about it and decided that the process is endothermic.

VIII.10. Bond enthalpies

During a chemical reaction a number of bonds will be formed or broken. **Forming bonds liberates energy and breaking bonds requires energy**. It would be useful to be able to attribute specific enthalpy changes to various bond changes. The sum of these enthalpy changes would equal the total enthalpy change.

Consider the breaking of the four C — H bonds in methane:

$$\begin{array}{c} H \\ | \\ H-C-H\,(g) \\ | \\ H \end{array} \rightarrow C(g) + 4H(g) \qquad \Delta H^{\circ} = -393.5 \text{ kJ mol}^{-1}$$

It is reasonable to assume that the energy required to break each C — H bond is the same and the same as is required to break a C — H bond in any other compound, and for all practical purposes this can be taken as true at this level.

For a diatomic molecule XY, the bond enthalpy is defined as the enthalpy change for the process:

$$X - Y(g) \rightarrow X(g) + Y(g)$$

Table VIII.1 lists some of the average bond enthalpies at 25°C.

It must be remebered these bond enthalpies can only be used as a guide. The actual value of a bond enthalpy will depend upon the nature of other atoms or groups joined to it.

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Table VIII.1 - Some average bond enthalpy at 25°C

Bond	ΔH kJ mol^{-1}
H — H	+436
C — C	+348
C = C	+612
C — F	+484
C — Cl	+338
C — Br	+275
C — I	+238

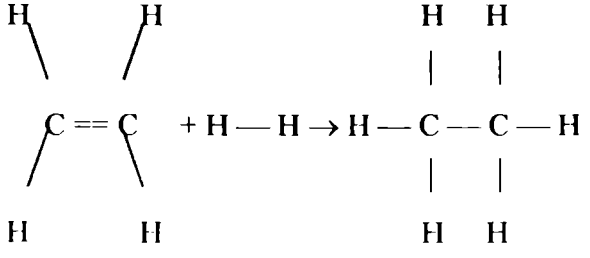
The enthalpy change is positive when a bond is broken and negative on making a bond. Bond enthalpies can be used to explain a number of facts from inorganic and organic chemistry.

E.g. The increased reactivity of phosphorus compared with nitrogen or the increased rate of substitution reactions for iodoalkanes compared with other haloalkanes.

The enthalpy change for atomisation can be estimated using bond enthalpies. for example, the atomisation of ethane C_2H_6 involves the breaking of one C — C bond and six C — H bonds. The enthalpy atomisation of there is:

$$= 1(C — C) + 6(C — H) = 348 + (6 \times 412) = +2820 \text{ kJ mol}^{-1}$$

Bond enthalpies can also be used to estimate likely enthalpy changes in chemical reactions, *e.g.* the hydrogenation of ethane



Using the information in Table VIII.1

Bond broken 1(C — C) + 1(H — H) Enthalpy change = +612 +436 = +1048 kJ

Bond formed 1(C — C) + 2(C — H) Enthalpy change = -348 +2(-412) = -1172 kJ

Net enthalpy change = 1048 - 1172 = -124 kJ

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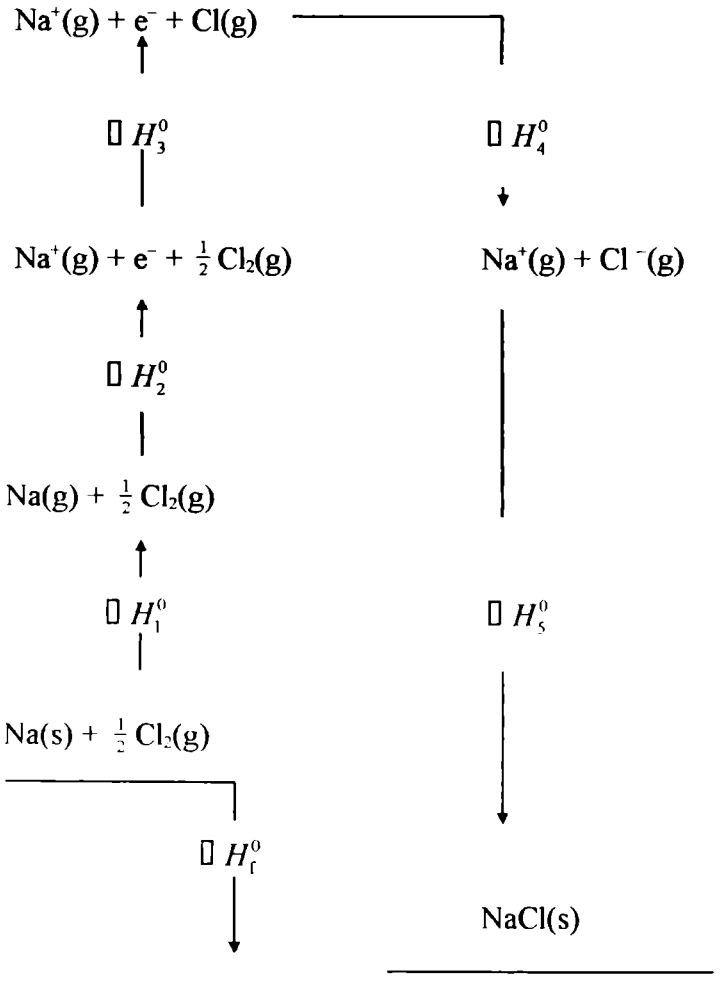
VIII.11. Born-Haber cycle

Lattice enthalpies cannot be determined directly but may be found indirectly by using an **energy diagram**. These diagrams are called **Born-Haber cycles**. The most common one seen on examination papers is the one for sodium chloride.

The standard enthalpy change when one mole of sodium chloride crystal is produced from sodium metal and chlorine gas can be determined experimentally and is, in fact, the standard enthalpy change of formation of sodium chloride

$$\Delta H_f^0 = -411 \text{ kJ mol}^{-1}$$

We can consider the various steps which are required to bring about this change:



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ΔH_1^0 corresponds to the **standard enthalpy change of atomisation** of sodium. It is the enthalpy change when one mole of solid sodium is converted to free sodium atoms. ΔH_1^0 = +108.4 kJ mol

ΔH_2^0 corresponds to the **first ionisation energy** of sodium *e.g.* the enthalpy change when one mole of electrons in their ground state is totally removed from 1 mole of sodium atoms in the gas phase. ΔH_2^0 = +500 kJ mol^{-1}

ΔH_3^0 corresponds to the **standard enthalpy change of atomisation** of chlorine. This is the enthalpy change when one mole of gaseous chlorine atoms is produced from chlorine molecules. ΔH_3^0 = +121 kJmol^{-1}

ΔH_4^0 corresponds to the **first electron affinity** of chlorine. This is the enthalpy change when one mole of chlorine atoms each accept one electron to form one mole of chlorine ions. ΔH_4^0 = -364 kJmol^{-1}

ΔH_5^0 corresponds to the **lattice enthalpy** sometimes called **lattice energy**)of sodium chloride.

By Hess's Law $\Delta H_f^0 = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0 + \Delta H_4^0 + \Delta H_5^0$

ΔH_5^0 = -776.4 kJmol^{-1}

An understanding of lattice enthalpy is extremely useful in various ways at A level:

(i) Substances with high lattice enthalpies will have melting points.

(ii) The solubility of an ionic compound will depend upon the relative values of the lattice and hydration enthalpies or energies.

(iii) Comparison of the calculated and experimental values lattice enthalpy gives an indication of the degree of covalent bonding in a compound.

(iv) Lattice enthalpies can be used to explain the non-existence of some compounds.

VIII.12. The stability of benzene

The enthalpy change of hydrogenation is the enthalpy change when one mole of hydrogen molecules is added to one mole of alkene. The enthalpy change of hydrogenation of cyclohexene is -120 kJ mol^{-1}.

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$+ \quad H_2 \quad \rightarrow$

If it is assumed that benzene contains three double bonds *i.e.* it is a triene, The enthalpy change of hydrogenation should be $3 \times (-120)$ kJ mol^{-1} *i.e.* -360 kJ mol^{-1}.

$+ \quad 3H_2 \quad \rightarrow$

The experimental value for the enthalpy change of hydrogenation of benzene is -208 kJ mol^{-1}. The difference between these two values (152 kJ mol^{-1}) is a measure of the extra stability of benzene compared with similar non-aromatic systems.

The standard enthalpy change of formation of benzene can be obtained by using the bond enthalpies in Table VIII.1 and assuming benzene is a cyclic triene.

$$\Delta H_f^0 = -(3 \times C=C + 3 \times C-C + 6 \times C-H) = -5352 \text{ kJ mol}^{-1}$$

The experimental value found by a Hess's law calculation is -5549 kJ mol^{-1}. The difference between these two values (197 kJ mol^{-1}) again is a measure of the stability of benzene. The difference between this value and the one obtained previously from hydrogenation calculations is probably due to the use of average values for bond enthalpies.

VIII.13. Second law of thermodinamics – entropy

The majority of reactions are exotermic and it was once believed that only exothermic reactions could take place. There is another factor which governs the feasibility of a reaction.The second factor is **enthropy**, which is related to the degree of randomness or disorder in the system.

If two gases in separate bulbs are allowed to come into contact, the gases mix and there is an increase in the disorder.

Given an opportunity, the disorder of a system, and hence its entropy, will spontaneously increase. The dissolving of an ionic crystal in water produces an increase in entropy. In the lattice the ions are regularly arranged. The dissolving of ammonium nitrate is an

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endothermic process and would not take place purely on energy considerations. There is, however, an increase in entropy which makes the process possible.

One statement of the second law of thermodinamics is that in any system a change that takes place spontaneously (*i.e.* of its own accord) will always involve in a particular process

divided by the temperature at which the process occurs *i.e.* $\Delta S = \frac{q}{T}$

Systems having perfect order *i.e.* the perfect ionic crystal lattice at 0 K, possess zero entropy. The entropy of a given mass of matter increases in the order:

$$\text{solid} \rightarrow \text{liquid} \rightarrow \text{gas}$$

The entropy of substances not possessing perfect order and of all substances at temperatures above 0 K will be greater than zero, *e.g.* the standard entropy S° (at 298 K and 1 atmosphere pressure) of water = 70 K^{-1} mol^{-1}.

The entropy change in a reaction can be found.

Example: Find ΔS° for the reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

given that the standard entropies of hydrogen, gaseous iodine and hydrogen iodine are +131, +261 and +207 J mol^{-1} K^{-1} respectively.

$$\Delta S^\circ = 2 \times S^\circ_{HI} - S^\circ_{H_2} - S^\circ_{I_2} = 414 - 131 - 261 = +22 \text{ J mol}^{-1} \text{ K}^{-1}$$

There is an increase in entropy and a spontaneous reaction is feasible, although no indication is given of the possible rate of reaction.

VIII.14. Free energy *G*

This is a measure of the useful work which can be obtained from a system (apart from volume changes).

A reaction can only proceed spontaneously ΔG is negative. ΔG depends upon ΔH and ΔS and they are related by the equation:

$$\Delta G = \Delta H - T\Delta S$$

Since for a reaction to proceed ΔG must be negative, for an endothermic reaction (ΔH positive), a reaction will take place only if $T\Delta S > \Delta H$. If ΔG is positive, no useful work can be obtained and the reaction is not feasible. If $\Delta G = 0$ the system will be in dynamic equilibrium.

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IX. REACTION KINETICS

IX.1. Introduction

Most O level courses now contain same work on rates of chemical reactions and the factors which affect the rate of reaction. The work on reaction kinetics becomes more significant at A level, because it is closely related to structure and to the mechanisms of reactions.

The factors which can effect the rate of reaction include:

(i) Physical state of reactants

(ii) Concentration (and gas pressure)

(iii) Temperature

(iv) Catalysts

(v) Light

These factors will be considered in turn.

IX.2. Physical state of reactants

The reaction between calcium carbonate and dilute hydrochloric acid is

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Figure IX.1 shows the graphs that would be obtained if equal masses of powered calcium carbonate and lamps of calcium carbonate were reacted separately with equal volumes of dilute hydrochloric acid of the same concentration (and excess). The volume of carbon dioxide collected were measured at intervals.

The volume of carbon dioxide collected in each case is the same because equal masses of calcium carbonate were used. It is produced very quickly with the powder and more slowly with the lumps. The reaction with the powder is faster because the powder has a larger surface area and the reaction takes place when the acid comes in contact with the surface.

IX.3. Concentration

This is probably the most important factor to understand at A level. During a reaction the reactants are used up and so the rate of reaction decreases.

The exact relationship between the rate of reaction and the concentration of the reactants in a particular reaction can only be determined experimentally. Most reactions take

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place in a series of steps and the rate of the overall reaction depends upon the rate of the slowest step, called the **rate determining step**.

It is vital for you to distinguish clearly the meaning of the terms **order of reaction** and **molecularity**. Few candidates understand the distinction and many questions test this. The order of reaction is determined experimentally. In the reaction

$$A + B \rightarrow C + D$$

experiment may show that the rate of reaction is proportional to the concentration of A to the power of x

$$i.e.\ \text{rate} \propto [A]^x$$

and also the rate of reaction may also be proportional to the concentration of B to the power of y

$$i.e.\ \text{rate} \propto [B]^y$$

The overall equation is therefore

$$\text{rate} = k[A]^x [B]^y$$

k is the **rate constant** and the overall equation is called the **rate equation**. In this example, the order of the reaction with respect to A is x and order with respect to B is y and the total order of reaction is $x + y$.

In the reaction between peroxodisulphate and iodide ions, the equation is

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The rate equation determined experimentally is

$$\text{rate} = k[S_2O_8^{2-}]\,[I^-]$$

and the total order is 2. The order is not related to the equation. The order may be integral *i.e.* 1, 2 or 3 etc, but it can also be fractional.

$$e.g. \quad H_2 + I_2 \rightarrow 2HI$$

$$\text{rate} = k[H_2]\,[I_2]$$

Order with respect to hydrogen = 1

Order with respect to iodine = 1

Total order of reaction = 1 + 1 = 2

$$H_2 + Br_2 \rightarrow 2HBr$$

$$\text{rate} = k[H_2]\,[Br_2]^{1/2}$$

Order with respect to hydrogen = 1

Order with respect to iodine = $\frac{1}{2}$

Total order of reaction = $1 + \frac{1}{2} = 1\frac{1}{2}$

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IX.4. Catalysts

A **catalyst** is a substance which alters the rate of a chemical reaction without being used up. The catalyst may be changed physically but the mass of catalyst is unchanged at the end of the reaction.

An example of a catalyst is manganese(IV) oxide in the decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

This is an example of a catalyst which speeds up a chemical reaction. A substance which slows down the rate of a reaction is called an inhibitor.

A catalyst does not alter the position of an equilibrium or increase the yield of products. It merely alters the rate at which the equilibrium is achieved or the products are obtained. A catalyst provides an alternative route with a lower activation energy barrier for the reaction. More molecules possess the lower activation energy and so the reaction is speeded up.

e.g. $2HI \rightarrow H_2 + I_2$

Activation energy without catalyst	183 kJ mol^{-1}
with gold catalyst	105 kJ mol^{-1}
with platinum catalyst	58 kJ mol^{-1}

There are two types of catalyst - **homogeneous catalysts** and **hetrogeneous catalysts**. A homogeneous catalyst is in same phase as the reactants *e.g.* the reaction between an organic acid and an alcohol is catalysed by the presence of hydrogen ion. A hetrogeneous catalyst is not in same phase *e.g.* manganese(IV) oxide is solid and hydrogen peroxide is a liquid. There are two theories of catalysis.

4.1 Intermediate compound theory

The catalyst reacts with one of the reactants to produce an intermediate compound which eventually produces the required product and regenerates the catalyst, *e.g.* manganese(IV) oxide and hydrogen peroxide.

The intermediate compound theory explains most examples of homogeneous catalysis.

4.2 Adsorption theory

A gas is adsorbed when its particles collide with and adhere to the catalyst surface. When gas molecules are adsorbed they are brought close together, and in a state which enables

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them to react together. On desorption the catalyst surface is available for further reaction. An example is the reaction of an alkene with hydrogen using a nickel catalyst.

The *d*-block elements and their compounds are good catalysts. The elements can exist in a variety of oxidation states and the metal surfaces are ideal for adsorption purposes.

In same reactions one of the products of the reaction acts as a catalyst for the reaction. For example, in the reaction of an ethanedioate (oxalate) with acidified potassium manganate(VII), the reaction has to be heated to about 60°C to get the reaction to start but the manganese(II) ions produced catalyse the reaction and the reaction continues even if the solution is cooled to room temperature. This is an example of what is called **autocatalysis**.

IX.5. Light

Some reactions are greatly affected by light. For example the reaction of hydrogen and chlorine is explosive in sunlight. The ultra violet light in sunlight splits some of the chlorine molecules into free chlorine atoms or chlorine **free radicals**.

$$Cl_2 \rightarrow 2Cl\bullet$$

Then a free radical chain reaction takes place producing hydrogen chloride.

$$Cl\bullet + H_2 \rightarrow HCl + H\bullet$$

$$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$$

The reaction between chlorine and methane is another example of a reaction affected by light.

IX.6. Methods of following the progress of a reaction

There are a number of methods which can be used to follow the progress of a reaction. These include:

(i) Measuring the volume of gas evolved at intervals using a gas syringe, *e.g.* in the reaction between calcium carbonate and hydrochloric acid.

(ii) Measuring the electrical resistance of the solution.

(iii) Measuring the change colour in the solution with a colorimeter.

(iv) Removing samples from the reacting mixture and titrating.

e.g. the hydrolysis of ethanoate with alkali. Portions of the reaction mixture are removed at intervals and titrated with dilute hydrochloric acid using phenolphthalein indicator.

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X. EQUILIBRIUM

X.1. Introduction

The topic of equilibrium is included in many O level syllabuses although many teachers leave it out or do not cover it adequately. It is an important topic which needs to be understood before Units XI and XII are attempted.

X.2. What is meant by chemical equilibrium?

The reaction between iron and steam is a reversible reaction

$$3Fe(s) + 4H_2O(g) \leftrightarrow Fe_3O_4(s) + 4H_2(g)$$

If steam is passed over heated iron in an open vessel, the forward reaction takes place and the iron oxide and hydrogen are produced. The steam displaces the hydrogen from the system, thereby limiting the ereverse reaction.

When hydrogen is passed over the heated iron oxide, iron and steam are produced.

An equilibrium is established, however, if iron and steam are heated in a *closed* container so the products cannot escape. In equilibrium, the concentrations of the two products and the two reactants remain constant providing external conditions are unchanged. The reactions have not stopped however. The rate of the forward reaction is equal to the rate of the reverse reaction and so the concentrations are unchanged. Using the term **dynamic equilibrium** is probably better because it emphasises the two reactions are continuing.

X.3. Quantitive approach to equilibrium

The **law of mass action** states that, at constant temperature, the rate of a reaction is proportional to the active mass of the reacting substances. For A level purposes, active mass is the same as concentration in mol dm^{-3}. The law of mass action applies to an equilibrium in a homogeneous system. The sign $\leftrightarrow$ shows the system can reach equilibrium.

In the equilibrium

$$aA + bB \leftrightarrow cC + dD$$

the equilibrium constant $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ at constant temperature.

By convention, the concentrations of products are divided by reactants.

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Equilibrium constants can be calculated using concentrations in mol dm^{-3}, and the equilibrium constant is represented by K_c Partial pressures can also be used to calculate equilibrium constants and the equilibrium constant is then represented by K_p.

Example:

$$CH_3COOH(l) + C_2H_5OH(l) \leftrightarrow CH_3COOC_2H_5(l) + H_2O(l)$$

Calculate K_c in terms of a,b and x if a moles of ethanoic acid and b moles of ethanol are mixed and left reach equilibrium and x moles of ethanoic acid are used up.

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

Initially	a moles	b moles	0	0
At equilibrium	$(a-x)$ moles	$(b-x)$ moles	x moles	x moles

In the total volume of the mixture is V dm^{-3}

$$[CH_3COOH] = \frac{a-x}{V} \qquad [C_2H_5OH] = \frac{b-x}{V} \qquad [CH_3COOC_2H_5] = \frac{x}{V} \qquad [H_2O] = \frac{x}{V}$$

(All units are mol dm^{-3})

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Substituting

$$K_c = \frac{\frac{x}{V} \cdot \frac{x}{V}}{\frac{a-x}{V} \cdot \frac{b-x}{V}} = \frac{x^2}{(a-x)(b-x)}$$

In this case, the volume of the mixture has no effect on the equilibrium constant.

If 1 mole of ethanoic acid and 1 mole of ethanol come to equilibrium, two third of mole of acid is used up. Calculate K_c.

$$\text{Substitute } a = 1 \text{ mole}, b = 1 \text{ mole}, x = \frac{2}{3} \text{ mole}$$

$$K_c = \frac{\frac{2}{3} \cdot \frac{2}{3}}{\frac{1}{3} \cdot \frac{1}{3}} = 4$$

The reactions involving gases, measuring the concentration at the same temperature are clearly defferent, although mathematically related. Just be consistent.

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X.4. Equilibrium in a heterogeneous system

The law of mass action can be modified to include heterogeneous systems. The common example is the heating of calcium carbonate in a closed system to prevent the escape of carbon dioxide

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$$

The vapour above the solid is a homogeneous system and

$$\frac{p_{CaO}}{p_{CaCO_3}} \times p_{CO_2} = \text{constant}$$

where p represents partial pressures. Thus at constant temperature the partial pressures of calcium carbonate and calcium oxide are constant. This is because the vapour pressures of solids are constant at constant temperature

$$K_p \propto p_{CO_2}$$

From this it follows that at any particular temperature, the partial pressure of carbon dioxide is constant.

X.5. Qualitative approach to equilibrium - Le Chatelier's principle

The way in which the position of an equilibrium will change if one of the conditions is changed is predicted qualitatively using **Le Chatelier's principle**.

Le Chatelier's principle states that if one of the conditions is changed, the position of equilibrium will alter in such a way as to tend to restore the original conditions.

Consider the equilibrium

$$A + B \leftrightarrow C + D$$

At equilibrium A, B, C, and D are present, and the concentrations of these substances remains constant providing conditions are unchanged. If the forward reaction is encouraged, a new equilibrium will be set up. In this equilibrium [C] and [D] will have increased and [A] and [B] will have decreased. The equilibrium is said to have 'moved to the right'.

A system 'moves to the left' if the new equilibrium established contains higher concentrations of A and B and lower concentrations of C and D.

The conditions which are commonly changed are:

(i) Concentrations of reactants or products.

(ii) Temperature.

(iii) Pressure. This is only important in reactions involving gases.

These conditions are considered separately.

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Concentration

If the product C is removed by liquefaction, escape into the atmosphere etc, the reverse reaction cannot occur. The position of the equilibrium moves to the right. If the concentration of A and B is increased, again the forward reaction is encouraged and again the equilibrium moves to the right.

Temperature

The change that takes place in an equilibrium when temperature is altered depends upon whether the forward reaction is exothermic or endothermic. If the forward reaction is exothermic, the reverse reaction will be endothermic. The equilibrium can be written

$$A + B \leftrightarrow C + D \qquad \Delta H \text{ is negative}$$

If the temperature of the system is raised, the equilibrium moves to the left as the endothermic process will tend to reduce the temperature, *i.e.* restore the original conditions. Conversely if the temperature is decreased, the equilibrium moves to the right.

Pressure

For a reaction involving gases, altering the pressure may cause a change in the position of the equilibrium.

For the reaction:

$$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$$

at 700°C, the number of moles of reactants and products are the same. Pressure has no effect on the position of the equilibrium.

For a reaction where there is an increase in the number of moles from reactants to products, increasing the pressure moves the equilibrium to the left. Where there is a decrease in the number of moles from reactants to products, increasing the pressure moves the equilibrium to the right.

X.6. The Haber process for manufacturing ammonia

Ammonia is produced industrially from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

This reaction is reversible. The yield of ammonia will depend upon the conditions under which the reaction is carried out. If the optimum conditions are sought the best yield of ammonia for the cost will give the maximum profit.

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Nitrogen is obtained by the fractional distillation of liquid air and hydrogen is obtained by the catalytic cracking of hydrocarbons or as a byproduct of the electrolysis of brine.

A mixture of nitrogen and hydrogen is dried and then compressed to 200 atmospheres. From the equation, and according to Le Chatelier's principle, the meximum yield of ammonia will be obtained by reducing the temperature. Unfortunately, lowering the temperature also decreases the rate of reaction and slows down the establishment of the equilibrium. The rate of the establishing the equilibrium can be increased by using a catalyst. Finely divided iron is used as a catalyst at approximately 500°C.

Under these conditions, only about ten per cent of nitrogen and hydrogen are converted to ammonia. The ammonia is removed from the gaseous mixture by cooling when the ammonia liquefies. The unreacted gases are recycled.

Much of the ammonia produced is subsequently converted to nitric acid or used to make ammonium compounds for fertilisers.

X.7. Contact process for manufacturing sulphuric acid

The Contact process involves three chemical reactions.

(i) Sulphur or a sulphur-containing mineral is burnt in air to produce sulphur dioxide.

$$S(s) + O_2(g) \leftrightarrow SO_2(g)$$

$$2ZnS(s) + 3O_2(g) \leftrightarrow 2ZnO(s) + 2SO_2(g)$$

or

(ii) The sulphur dioxide is reacted with further oxygen to produce sulphur(VI) oxide (sulphur trioxide).

$$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g) \qquad \Delta H = -192 \text{ kJ mol}^{-1}$$

(iii) Sulphur trioxide is dissolved in concentrated sulphuric acid and the resulting solution is mixed with the correct quantity of water.

$$H_2SO_4(l) + SO_3(g) \leftrightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \leftrightarrow 2H_2SO_4(l)$$

Only stage 2 is a reversible reaction so it is the conditions in stage 2 which will determine the final yield of sulphuric acid.

The forward reaction in Stage 2 is exothermic. According to Le Chatelier's principle, low temperatures will favour the maximum yield of sulphur trioxide. Again, lowering the temperature will slow the establishment of the equilibrium. A catalyst of vanadium(V) oxide is used to speed up the process and a compromise the temperature of 450 - 500°C is used.

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In theory, the yield of sulphur(VI) oxide will be increased by increasing the pressure since there is a decrease in the number of molecules from left to right. In practice the extra yield obtained is so small that the extra cost could not be justified. The process is carried out at a little more than atmospheric pressure, to ensure a good flow of gas.

In the final stage the reaction of sulphur trioxide with water directly is too exothermic causing the acid to boil. The sulphur trioxide is dissolved in concentrated sulphuric acid to form oleum (or fuming sulphuric acid) which can be mixed with water to form concentrated sulphuric acid.

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XI.1. Introduction

This unit concernsvarious topic related to acids and bases. The terms acid and base should be familiar to you from O level. At O level and acid might be defined as a compound containing replaceable hydrogens

e.g.	H_2SO_4	$NaHSO_4$	$NaSO_4$
	sulphuric acid	*sodium hydrogensulphate*	*sodium sulphate*

An acid and base react to form a salt and water only. For A level, the definitions of acid and base must be more clearly stated.

One important distinction for you to understand is between a strong and weak acid. A **strong acid** is an acid which is highly dissociated into ions and a **weak acid** is only slightly dissociated into ions.

XI.2. Definitions of acids and bases

Bronsted and Lowry defined an **acid** as a **proton donor** and a **base** as a **proton acceptor**. A proton is the same a sa positively hydrogen ion (H^+) . In practice, H^+ ions do not exist in solution and are more likely to exist as H_3O^+.

The equation for the ionisation of hydrochloric acid is:

$$HCl(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + Cl^-(aq)$$

Hydrochloric acid is an acid because it loses an H^+ion to form a Cl^- ion. Water is a base because it accepts H^+ions to form H_3O^+ions.

Looking at the reverse reaction, H_3O^+ions lose H^+ions in forming H_2O and, therefore $H_3O^+$is acting as an acid. Chloride ions accept H^+ions to form HCl and, therefore, act as a base. The $H_3O^+$is called the **conjugate acid** and Cl^- the **conjugate base** (*i.e.* the acid and base for the reverse process).

In the case of a general acid HA

$$HA(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^-(aq)$$

The position of this equilibrium depends upon the strength of the acid. For a strong acid such as Hcl the equilibrium lies well to the right, *i.e.* the acid may be considered as

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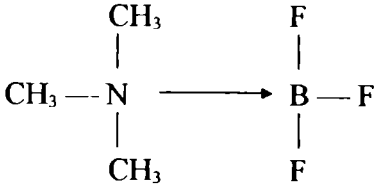
completely ionised. In such a case the base Cl^- is very weak base. With a weak acid the equilibrium lies well to the left. A^- is a fairly strong base.

Water can act as an acid:

$$\underset{\textit{base}}{NH_3} + \underset{\textit{acid}}{H_2O} \leftrightarrow \underset{\textit{conjugate acid}}{NH_4^+} + \underset{\textit{conjugate base}}{OH^-}$$

Lewis widened the definition of acid and base by defining an acid as an **electron pair acceptor**. This definition includes examples of acids and bases which would not be recognised using the other definitions. For example the reaction between trimethylamine and boron trifluoride forms a solid salt.



Trimethylamine has an electron pair which can be donated to the boron trifluoride which is electron deficient because it only has six electrons in the outer shell.

Trimethylamine acts as a Lewis base and boron trifluoride is a Lewis acid. Aluminium chloride acts as a Lewis acid.

XI.3. Ostwald's dilution law

Since the ionisation of weak acids and bases are equilibrium processes, the law of mass action can be applied to them at constant temperature.

For example, consider the dossociation of 1 mole of a weak acid HA. If the volume of the solution containing one mole of acid is V dm^3 and α is the degree of dissociation, then

	HA	$\leftrightarrow$	H^+	+	A^-
Before ionisation	1 mole		0		0
After ionisation	$1-\alpha$ mole		α mole		α mole
	$[HA] = \frac{1-\alpha}{V}$ mole dm^{-3}		$\frac{\alpha}{V}$ mole dm^{-3}		$\frac{\alpha}{V}$ mole dm^{-3}

Applying the law of mass action.

$$K = \frac{[H^+][A^-]}{[HA]}$$

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$$K = \frac{\alpha^2}{(1-\alpha)V} \text{ mole dm}^{-3}$$

This expression is called **Ostwald's dilution law**. The equilibrium constant in this cases is the **dissociation constant**. For very weak electrolytes, where little dissociation takes place, $(1 - \alpha)$ is approximately equal to 1 and the expression simplifies to

$$K = \frac{\alpha^2}{V} \text{ or } K = \alpha^2 c$$

where V is the volume containing one mole and c is the concentration in mole dm^{-3}.

Although the degree of dissociation of the acid changes with dilution, the value of K is unchanged at constant temperature.

Example: The degree of dissociation of 0.02M benzenecarboxylic acid, C_6H_5COOH, is 0.056 at 25°C. Calculate the dissociation constant of the acid at this temperature.

$$C_6H_5COOH \leftrightarrow C_6H_5COO^- + H^+$$

Using Ostwald's dilution law

$$K = \frac{\alpha^2}{(1-\alpha)V} \qquad V = 50 \text{ dm}^{-3}$$

$$K = \frac{0.056^2}{(1-0.056)50} = 0.000063 \text{ mole dm}^{-3}$$

XI.4. Ionic Product of water

Even if water is purified by repeated distillations, the electrical conductivity never falls to zero. This is because of **self-ionisation** of water. This can be represented either by

$$2H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-(aq)$$

or

$$H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)$$

Using the simpler equation

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Only a few molecules of water ionise and $[H_2O]$ can be regarded as constant at constant temperature.

$$K_w = K_w \times \text{constant} = [H^+]\,[OH^-]$$

This is called the **ionic product** of water.

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At 25°C, K_w 1×10^{-14} mol^2 dm^{-6} and becuase, from the equation, the concentrations of H^+ and OH^- are equal:

$$[H^+] = [OH^-] \quad 1 \times 10^{-7} \text{ mol dm}^{-3}$$

In any aqeous solution the product of the concentration of H^+ and OH^- is 1×10^{-14} mol^2 dm^{-6}. In a neutral solution both $[H^+]$ and $[OH^-]$ equal 1×10^{-7} mol dm^{-3}.

The ionic product is useful in A level questions. If either the $[OH^-]$ or $[H^+]$ is known, the other one can be calculated.

e.g. A solution contains $[OH^-] = 10^{-1}$ mol dm^{-3}

Since $[H^+]\,[OH^-] = 1 \times 10^{-14}$ mol^2 dm^{-6} and $[OH^-] = 10^{-1}$ mol dm^{-3} $[H^+] = 10^{-13}$ mol dm^{-3}

XI.5. pH

A solution which is neutral contains

$$[H^+] = [OH^-] = 10^{-7} \text{ mol dm}^{-3}$$

If a solution is acidic

$$[H^+] > [OH^-]$$

and if the solution is alkaline

$$[H^+] < [OH^-]$$

The concentration of the ions are all very small

e.g. a weak acid might have $[H^+] = 6.28 \times 10^{-6}$ mol dm^{-3}

The system of pH is designed to simplify these values by removing the awkward negative indices. pH is defined as $-\log_{10}[H^+]$.

A solution with $[H^+] = 10^{-7}$ mol dm^{-3} has a pH = 7. This is a neutral solution.

Solutions that are acidic have a pH less than 7. A solution of hydrochloric acid (0.1 mol dm^{-3}) ionises to produce 0.1 mol dm^{-3} of H^+ ions (10^{-1} mol dm^{-3}). The pH of this solution is 1 (*i.e.* $-\log_{10} 10^{-1}$).

A solution with $[H^+] = 6.28 \times 10^{-6}$ mol dm^{-3} has a pH of 5.20.

Solutions in which $[OH^-]$ is greater than $[H^+]$ are alkaline and have a pH greater than 7. A solution of sodium hydroxide (0.1mol dm^{-3}) ionises to produce 0.1 mol dm^{-3} of OH^- (10^{-1} mol dm^{-3}).

Using the ionic product of water,

$$[H^+]\,[OH^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

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$$[H^+] = 10^{-13} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}[H^+] = 13$$

For a weak acid HA in water, the equilibrium in the solution will be

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

The equilibrium constant K_c is given by

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

In the dilute solution $[H_2O]$ is large and effectively constant.

$$\frac{[H_3O^+][A^-]}{[HA]} = K_c \times \text{constant} = K_a$$

K_a (called the **acid dissociation constant**) is the measure of the strength of an acid. For example for methanoic acid $K_a = 1.6 \times 10^{-4}$ mol dm^{-3} ; it is obvious that the ionosation of this acid is small, and many organic acids have even smaller values.

All K_a values are very small and it is convenient to record the strngths of acids as pK_a values. (This is similar to use of pH for recording $[H^+]$).

$$pK_a = -\log_{10} K_a$$

The important thing to remember is that the **smaller** the values of pK_a, the larger is the values of K_a and the **stronger** is the acid.

The equilibrium that exists when a base is added to water is

$$B + H_2O \leftrightarrow BH^+ + OH^-$$

Again $[H_2O]$ is approximately constant

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b is called the **base dissociation constant**. It is a measure of the strength of a base and, for convenience, it is usually expressed as a pK_b values. The **smaller** the value of pK_b the **stronger** is the base.

XI.6. Indicators and acid–alkali titrations

Most indicators for acid–alkali titrations are weak acids or bases. Phenolphthalein is a weak acid and it dissociates

$$H_2O + HA \leftrightarrow H_3O^+ + A^-$$

colourless *pink*

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HA exists in acid solution and A^- in alkaline solution. If acid is added to the equilibrium mixture, the equilibrium moves to the left and the solution turns colourless. Addition of alkali removes H_3O^+ ions and moves equilibrium to the right turning the solution pink.

Methyl orange is a weak base which dissociates

$$BOH \leftrightarrow B^+ + OH^-$$

yellow *red*

BOH exists in alkaline solution and B^+ in acid solution. For a substance to be a good indicator, the two forms (HA and A^- for phenolphthalein and BOH and B^+ for methyl orange) must be different colours for the indicator to function adequately.

The weak acids and bases which act as indicators have varying K_a and K_a values and, in consequence, they change colour at different characteristic pH values.

Table XI.1 lists the common indicators, their colour change and the pH range at which the colour change occurs.

Table XI.1 - Color changes of some common indicators

Indicator	*Acid solution*	*Approx. pH*	*Alkali solution*
methyl orange	orange	4	yellow
methyl red	red	5	yellow
litmus	red	7	blue
phenolphthalein	colourless	9	red

In chosing the indicator for an acid-alkali titration it is important to consider the pH at which the indicator changes colour.

(i) Strong acid – strong base
(ii) Weak acid – strong base
(iii) Strong acid – weak base
(iv) Weak acid – weak base

Figure XI.1 shows curves of pH during titrations of the four types of acid-alkali titrations.

(i) Strong acid – strong base

E.g. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

0.1M sodium hydroxide solution is added to 25 cm^3 of 0.1M hydrochloric acid. Initially, the pH of the solution is 1 and the pH increases as alkali is added. When 25 cm^3 of sodium hydroxide solution is added the solution is exactly neutral (pH 7) and further addition of sodium hydroxide solution gives a pH greater than 7 as all the acid is used up and the alkali is in excess. A suitable indicator changes colour on the vertical portion of the graph (between 3

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and 11). On the vertical portion, there is a rapid change in pH with addition of a small amount of alkali.

(ii) Weak acid – strong base

E.g. $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

0.1M ethanoic acid has a pH between 2 and 3 (not 1 as with a strong acid because it is less completely ionised). On addition of 0.1M sodium hydroxide the curve in *(b)* is obtained. The vertical portion is between 7 and 10 and phenolphthalein is the best indicator to use.

(iii) Strong acid – weak base

E.g. $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

This time the vertical portion of the graph is between about 3 and 7 and methyl orange or methyl red is suitable.

(iv) Weak acid – weak base

E.g. $CH_3COOH(aq) + NH_3(aq) \rightarrow CH_3COONH_4(aq)$

There is no vertical portion on the graph. There is no sharp change in pH and no indicator is suitable.

It is possible to use different indicators for the same titration to detect different end points. For example, the reaction of sodium carbonate with dilute hydrochloric acid has the following overall equation.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

This is detected by methyl orange or methyl red.

Phenolphthalein, however, will detect the end point of the reaction.

$$Na_2CO_3(aq) + HCl(aq) \rightarrow NaHCO_3(aq) + NaCl(aq)$$

This end point requires only half of the volume of acid compared to that with methyl orange or methyl red as indicator.

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XII SALT HYDROLYSIS AND BUFFER SOLUTIONS

XII.1. Salt hydrolysis

The unit covers three important topics related to ionic equilibrium.

The first task here is to recognise that a question is a salt hydrolysis question.

When a salt is dissolved in water, the resulting solution may be acid, alkaline or neutral. This is because the salt may have reacted to some extent with the water. This hydrolysis produces an acid and an alkali but they may not be of equal strength. There are four types of salt that should be considered.

Salt of a strong acid and a strong base

E.g. sodium chloride. Sodium chloride is completely ionised in solution to form $Na^+(aq)$ and $Cl^-(aq)$. $H_3O^+(aq)$ and $OH^-(aq)$ are also present from the ionisation of a few of the water molecules. There is no interaction between the sodium and chloride ions and the water and as a result the concentrations of $H_3O^+(aq)$ and $OH^-(aq)$ are the same and the solution is exactly neutral.

Salt of a strong acid and a weak base

E.g. ammonium chloride or iron(III) chloride. In a solution of ammonium chloride, there is a reaction between ammonium ions in the solution and the solvent to produce additional $H_3O^+(aq)$ ions.

$$NH_4Cl(s) \rightarrow NH_4^+(aq) \text{ and } Cl^-(aq)$$

and

$$NH_4^+(aq) + H_2O(l) \leftrightarrow NH_3(aq) + H_3O^+(aq)$$

The resulting solution is acidic becuase of an excess of $H_3O^+(aq)$ ions over $OH^-(aq)$ ions.

A solution of iron(III) chloride in water is appreciably acidic. It will react rapidly with magnesium to produce hydrogen.

Salt of a weak acid and a strong base

E.g. sodium ethanoate. The ionisation of sodium ethanoate produces $CH_3COO^-(aq)$ and $Na^+(aq)$. The resulting solution is alkaline, however, because of reaction between the ethanoate ions and the water to preoduce an excess of $OH^-(aq)$ ions.

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$$CH_3COONa(s) \leftrightarrow CH_3COO^-(aq) + Na^+(aq)$$

$$CH_3COO^-(aq) + H_2O(l) \leftrightarrow CH_3COOH(aq) + OH^-(aq)$$

Salt of a weak acid and a weak base

E.g. ammonium ethanoate. Ammonium ethanoate is ionised in solution to produce $NH_4^+(aq)$ and $CH_3COO^-(aq)$ ions. Both of these ions react with water.

$$NH_4^+(aq) + H_2O(l) \leftrightarrow NH_3(aq) + H_3O^+(aq)$$

$$CH_3COO^-(aq) + H_2O(l) \leftrightarrow CH_3COOH(aq) + OH^-(aq)$$

Whether the final solution is slightly acidic, slightly alkaline or neutral depends upon the position of the two equilibria. In fact this solution is almost neutral.

XII.2. Buffer solutions

In this book only a qualitative account of the subject is given.

A **buffer solution** is a solution of constant pH. The pH os the solution will not change appreciably if the solution is contaminated with traces of acid or alkali.

An acidic buffer solution (*i.e.* with pH less than 7) is prepared by mixing together definite amounts of a weak acid and the sodium or potassium salt of the same acid, *e.g.* ethanoic acid and sodium ethanoate.

An alkaline buffer (*i.e.* with pH greater than 7) is prepared by mixing a weak base and a soluble salt of the base, *e.g.* ammonia solution and ammonium chloride.

The most frequent mistake at A level is to fail to appreciate that a weak acid or base is required to make a buffer solution. Statements such as 'hydrochloric acid and sodium chloride can be used to make a buffer solution' are common.

The mixture of ethanoic acid and sodium ethanoate acts as a buffer as follows:

$$CH_3COO^-(aq) + H_2O(l) \leftrightarrow CH_3COOH(aq) + OH^-(aq)$$

$$CH_3COONa(s) \leftrightarrow CH_3COO^-(aq) + Na^+(aq)$$

The resulting mixture contains a large concentration of ethanoate ions, most of which come from the sodium ethanoate.

If $H_3O^+(aq)$ ions are added, the equilibrium in the first equation is disturbed and moves to the left in order to reduce the $H_3O^+(aq)$ concentration. This is in accordance with Le Chatelier's

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principle and the concentration of $H_3O^+(aq)$ remains unchanged. The acidity is therefore unchanged.

If OH (aq) ions are added, they remove the $H_3O^+(aq)$ ions from the solution.

$$H_3O^+(aq) + OH\ (aq) \rightarrow 2H_2O(l)$$

The equilibrium in the first equation is disturbed by the removal of $H_3O^+(aq)$. The equilibrium moves to the right to produce more $H_3O^+(aq)$ and restore the pH of the solution. The mixture of ammonia solution and ammonium chloride acts as abuffer solution as follows:

$$NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)$$

$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

This buffer solution contains a large concentration of $NH_4^+(aq)$ ions. Most of these ions come from the ammonium chloride which is completely ionised.

If $OH^-(aq)$ ions are added, the equilibrium in the first equation moves to the left in accordance with Le Chatelier's principle. This reduces the concentration of the $OH^-(aq)$ and restores the original pH. If $H_3O^+(aq)$ ions are added, they remove $OH^-(aq)$ from the solution. The equilibrium moves to the right to produce more $OH^-(aq)$.

XII.3. Solubility product

The ideas of equilibrium can be applied to the equilibrium between an almost insoluble solid and its ions in solution. This leads to the concept of **solubility product** which explains the conditions under which precipitation from a solution will occur.

For example, silver chloride AgCl is a suitable sparingly soluble salt.

$$AgCl(s) \leftrightarrow AgCl(aq) \leftrightarrow Ag^+(aq) + Cl\ (aq)$$

An equilibrium is established when silver chloride is added to water. Using the ideas of equilibria, the following expression can be obtained

$$K_s = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

[AgCl] strictly represents the concentration of silver chloride in solution and this remains constant at constant temperature, as long as any solid remains in contact with the solution.

$$K_s = [Ag^+]\,[Cl^-] = 2 \times 10^{-10}\ mol^2\ dm^{-6}$$

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where K_s is called the **solubility product**. The solubility product is the maximum value of the ionic product of Ag^+ and Cl^- ions that can exist in solution without precipitation occuring.

If the product of the ionic concentrations exceeds this maximum value precipitation will occur.

Another common example is silver chromate(VI), Ag_2CrO_4, and the solubility product for silver chromate is

$$K_s = [Ag^+]^2 [CrO_4^{2-}] = 3 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

For the sparingly soluble electrolyte A_xB_y the equilibrium is:

$$A_xB_y(aq) \leftrightarrow xA^{y+}(aq) + yB^{x-}(aq)$$

and the solubility product is

$$K_s = [A^{y+}]^x [B^{x-}]^y$$

The most frequent mistake with solubility product is to try to apply it to solids that are readily soluble. For example, when dry hydrogen chloride is bubbled through a satured solution of sodium chloride, sodium chloride crystals precipitate out. Many candidates would state that the solubility product of sodium chloride had been exceeded and precipitation occurs. This statement is incorrect as the solubility product of sodium chloride is meaningless, since sodium chloride is so soluble.

The observation is explained by the **common ion effect**. The equation for the solubility of sodium chloride is:

$$NaCl(s) \leftrightarrow Na^+(aq) + Cl^-(aq)$$

Addition of a large concentration of chloride ions (from the hydrogen chloride) moves the equilibrium to the left and sodium chloride precipitates.

Solubility product can be used to calculate the solubility of a sparingly soluble solid in water. For example, the solubility product of iron(III) hydroxide $Fe(OH)_3$ at 25°C is 8×10^{-40} mol^4 dm^{-12}. Calculate the solubility product of iron(III) hydroxide in a satured solution at 25°C. ($A_r(Fe) = 56.0$, $A_r(O) = 16.0$, $A_r(H) = 1.0$)

Relative molecular mass of iron(III) hydroxide = $56 + (3 \times (16 + 1)) = 107$

$$K_s = [Fe^{3+}] [OH^-]^3 = 8 \times 10^{-40} \text{ mol}^4 \text{ dm}^{-12}$$

$$Fe(OH)_3 \leftrightarrow Fe^{3+} + 3OH^-$$

Now $3[Fe^{3+}] = [OH^-]$

Substitute

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$$K_s = [Fe^{3+}] (3[Fe^{3+}])^3$$

$$= 27[Fe^{3+}]^4 = 8 \times 10^{-40}$$

$$[Fe^{3+}]^4 = 0.3 \times 10^{-40}$$

$$[Fe^{3+}]^4 = = 0.74 \times 10^{-10} \text{ mol dm}^{-3}$$

Mass of of iron(III) hydroxide dissolving per $dm^3 = 0.74 \times 10^{-10} \times 107 = 7.9 \times 10^{-9}$ g.

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XIII. OXIDATION AND REDUCTION

XIII.1. Introduction

In an elementary chemistry course, oxidation might be defined as a chemical reaction where oxygen is gained or hyudrogen is lost. Reduction is the opposite process to oxidation. It is, therefore, a reaction where oxygen is lost or hydrogen is gained.

For example when hydrogen is passed over heated copper(II) oxide, the following reaction takes place.

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$$

The copper(II) oxide loses oxygen and is reduced while hydrogen gaines oxygen and is oxidised. The hydrogen, which is required to reduce the copper(II) oxide, is called to reducing agent (remember the reducing agent is oxidised). The copper(II) oxide is an oxidising agent and is itself reduced.

The elementary treatment of oxidation is easy to understand but it does not include all possible oxidation and reduction reactions. Oxidation and reduction occur together and the term **redox reaction** means a reaction where oxidation and reduction take place.

XIII.2. Oxidation and reduction in terms of electron transfer

Defining oxidation and reduction in terms of electron loss and gain is more useful, for not all reactions involve oxygen and hydrogen.

Oxidation is a process where electrons are lost and reduction where electrons are gained (Remember: **leo** - **l**oss of **e**lectrons **o**xidation). A reducing agent is an electron donor and an oxidising agent is an electron acceptor.

For example, the elementary definition in XIII.1 is too simplistic to cope with the reaction of chloride with iron(II) chloride solution which is not obviously a redox reaction. The equation is

$$2FeCl_2(aq) + Cl_2(g) \rightarrow 2FeCl_3(aq)$$

Writing this equation as an ionic equation gives

$$2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$

There are two processes taking place here:

(i) Iron(II) ions Fe^{2+} are losing electrons to form iron(III) ions

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$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e$$

(ii) Chlorine atoms are gaining electrons to form chloride ions.

$$Cl_2(g) + 2e \rightarrow 2Cl\ (aq)$$

During the reaction, iron(II) ions lose electrons and are therefore oxidised and chlorine which gains electrons is reduced. Chlorine is the electron acceptor and is therefore the oxidising agent and the iron(II) ions the reducing agent (electron donor).

From this example it should be noted that ionic equations and the simple ionic equations (like*(i)* and *(ii)* above), called **half equations**, are useful when considering oxidation and reduction.

XIII.3. Common oxidising agents

In this section the common oxidising agents are listed. It is a good idea to learn the half equation which accompanies each oxidising agent. In all of these equations electrons are shown on the left hand side since all oxidising agents are electron acceptors. (NB For the sake of simplicity the ion H_3O^+ is represented in these equations by $H^+(aq)$.)

oxygen $O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$

chlorine $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

bromine $Br_2(g) + 2e^- \rightarrow 2Br^-(s)$

iodine $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

manganate(VII) in acid solution

$$MnO_4^-(aq) + 8H^+(aq) + 5e \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

manganate(VII) in alkaline solution

$$MnO_4^-(aq) + 2H_2O(l) + 3e \rightarrow MnO_2(s) + 4OH^-(aq)$$

dichromate(VI) in acid solution

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

iron(II) salts

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$$

hydrogen ions

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

hydrogen peroxide (in the absence of another oxidising agent)

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$$

manganese(IV) oxide (in the presence of acid)

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$MnO_2(aq) + 4H^+(aq) + 2e \rightarrow Mn^{2+}(aq) + 2H_2O(l)$

concentrated sulphuric acid

$2H_2SO_4^{2-}(l) + 2e^- \rightarrow SO_4^{2-}(aq) + 2H_2O(l) + SO_2(g)$

You will find other examples elsewhere in the book.

XIII.4. Common reducing agents

In a similar way, a list of reducing agents can be drawn up. In all of these half equations, electrons appear on the right hand side of the equation as reducing agents are electron donors.

metals $M(s) \rightarrow M^{n+}(aq) + ne^-$

e.g. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

iron(II) salts

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

acidified potassium iodide

$2I^-(aq) \rightarrow I_2(aq) + 2e^-$

thiosulphate

$2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$

ethanedioic acid and ethanedioates (oxalic acid and oxalates)

$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$

hydrogen sulphide and sulphides

$S^{2-}(aq) \rightarrow S(s) + 2e^-$

sulphurous acid (sulphuric(IV) acid)

$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$

hydrogen peroxide (in the presence of a strong oxidising agent)

$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e$

tin(II) ions in hydrochloric acid

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

hydrogen $H_2(g) + O^{2-}(s) \rightarrow H_2O(l) + 2e^-$

carbon $C(s) + O^{2-}(s) \rightarrow CO(g) + 2e^-$

carbon monoxide

$CO(g) + O^{2-}(s) \rightarrow CO_2(g) + 2e^-$

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XIII.5. Using ionic half equations to write full ionic equations

Combination of two ionic half equations, one representing an oxidising action and one representing a reducing action, will produce a full ionic equation. This could be used, if required, to produce a molecular equation. Remember, however, that it is possible to write equations for reactions which do not in fact take place. Whether a reaction takes place depends upon the standard electrode potentials.

E.g. reaction of acidified potassium manganate(VII) with iron(II) sulphate solution. Write out the relevant half equations.

OA $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

RA $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

On combining these equations the electrons must cancel out. Multiply the RA equation by 5 and add

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

In this equation, manganate(VII) acts as the oxidising agent and iron(II) ions as the reducing agent.

The reaction of acidified potassium manganate(VII) with acidified potassium iodide. Write the relevant half equations.

OA $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

RA $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

In order to remove the electrons, multiply the OA equation by 2 and RA by 5 and add

$$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5I_2(aq)$$

XIII.6. Recognising oxidation and redustion from an ionic equation

If you are given a full ionic equation it is possible to split it up into its constituent half equations.

E.g. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

The half equations are:

OA $2H^+(aq) + 2e^- \rightarrow H_2(g)$

RA $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

In this reaction $H^+(aq)$ ions are reduced and zinc atoms are oxidised.

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XIII.7. Hydrogen peroxide as oxidizing and reducing agent

Hydrogen peroxide can act as an oxidising agent or a reducing agent according to the conditions.

In the absence of a stronger oxidising agent, hydrogen peroxide acts as an oxidising agent. *E.g.* hydrogen peroxide and acidified potassium iodide

OA $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

RA $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Add $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$

When a stronger oxidising agent is present, hydrogen peroxide then acts as a reducing agent.

OA $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

RA $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$

Multiply OA equation by 2 and the RA equation by 5 and add:

$2MnO_4^-(aq) + 16H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g) + 10H^+(aq)$

This equation can be slightly simplified. There are $16H^+(aq)$ on the left hand side and $10H^+(aq)$ on the right hand side. An equation should show change and $10H^+(aq)$ can be subtracted from both sides.

$2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$

If the two equations for hydrogen peroxide are written down and added together we get

OA $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

RA $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$

Add $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

This equation represents the decomposition of hydrogen peroxide into water and oxygen. The reaction can be regarded as the disproportionation of hydrogen peroxide with hydrogen peroxide acting simultaneously as oxidising and reducing agent.

XIII.8. Oxidation state (or oxidation number)

The system of **oxidation state** (or **oxidation number**) has been devised to give a guide to the extent of oxidation or reduction in a species. The system is without direct chemical

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foundation, but is extremely useful, being appropriate to both ionic and covalently bonded species.

The oxidation state can be defined simply as the number of electrons which must be added to a positive ion to get a neutral atom or removed from a negative ion to get a neutral atom.

E.g. $Fe^{2+}(aq)$ - two electrons have to be added and the oxidation state is +2.

Cl (aq) - one electron has to be removed and the oxidation state is -1.

It is relatively easy to understand for simple ions because the electrons are definitely associated with certain ions.

For covalent species it is assumed that the electrons in the covalent bond actually go to the atom which is most electronegative. For example in ammonia, NH_3, nitrogen is the more electronegative element and it is assumed that the three electrons (one from each hydrogen atom) are associated with the nitrogen atom. Nitrogen, therefore (like nitrogen in N^{3-}) has an oxidation state of -3 and hydrogen +1.

The system will be clear with practice but the following rules are worth remembering.

(i) The oxidation state of all elements uncombined is zero. therefore the oxidation state of oxygen in oxygen gas is zero.

(ii) The algebraic sum of the oxidation states of the elements in a compound is always zero.

E.g. in NH_3			
	N	OS	-3
	H	OS	+1
	H	OS	+1
	H	OS	+1
			0

(iii) The algebraic sum of the oxidation states of the elements in an ion is equal to the charge on the ion.

E.g. in CO_3^{2-}			
	C	OS	+4
	O	OS	-2
	O	OS	-2
	O	OS	-2
			-2

(iv) The oxidation state of oxygen is -2 (except in oxygen gas and peroxides)

(v) The oxidation state of hydrogen is +1 (except when combined with Group I or II metals as hybrides).

In chemical names the oxidation state of a particular species may be shown in Roman numerals in brackets if there is chance of any uncertainty. In these cases the sign is not given.

E.g. iron(III) chloride - iron is in oxidation state +3

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tetracarbonylnickel(0) - nickel is in oxidation state zero.

If during a chemical reaction a species changes its oxidation state, then oxidation and reduction are taking place. An increase in oxidation state corresponds to oxidation and a decrease to reduction.

E.g. the reaction of chlorine with hydrogen sulphide

$$Cl_2(g) + H_2S(g) \rightarrow 2HCl(g) + S(s)$$

This could be written in two ionic half equations

OA $\quad Cl_2(g) + 2e^- \rightarrow 2Cl^-(g)$

RA $\quad S^{2-}(g) \rightarrow S(s) + 2e^-$

Add together $\quad Cl_2(g) + S^{2-}(g) \rightarrow 2Cl^-(g) + S(s)$

The oxidation state of chlorine in Cl_2 is zero (because it is an element) and in HCl is -1. (Remember H is usually in OS +1 and the sum must be zero.)

The chlorine therefore is reduced because the oxidation state is reduced from 0 to -1. Similarly, the oxidation state increases from -2 in H_2S to zero in S. The sulphur is oxidised as there is an increase in oxidation state.

With *d*-block elements, a variety of oxidations states are possible for each element.

APPLICATIONS

In this unit the subject is developed quantitatively by the introduction of the concept of **electrode potential**.

XIII.9. Electrochemical cells

When a metal rod is dipped into a solution of metal ions an equilibrium is set up. There is a tendency for the metal to form positive metal ions and go into solution. There is also a tendency for metal ions in solution to gain electrons from the metal and be deposited. This can be summarised as:

$$M(s) \leftrightarrow M^{n+}(aq) + ne^-$$

Whether the metal acquires an overall positive or negative charge depends upon the position of equilibrium. This depends upon the particular metal. With reactive metals the equilibrium lies well to the right hand side.

A metal dipping into a metal salt solution is called a **half cell**. Combining two half cells together can produce an **electrochemical cell**.

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For example an electrochemical cell is described bellow:

A zinc rod dips into a solution of zinc sulphate and copper rod dips into a solution of copper(II) sulphate. The porous pot allows ions to move without the solutions mixing freely. This cell is called the **Daniell cell**.

In this cell the following reactions take place

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The overall equation is obtained by addition.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

The chemicals possess a certain amount of chemical energy that is converted into electrical energy in the cell. The cell stops working when either the zinc rod or the copper(II) sulphate solution is used up.

The zinc ions go into solution. The lectrons that are released flow through the external circuit to the copper electrode and are used to deposit the copper.

The meximum potential difference between the two electrodes is known as the **electromotive force** (emf). If both solutions have concentrations of 1 mol dm^{-3}, the emf of the Daniell cell is 1.1 volts. The maximum potential difference is obtained when there is a large resistance in the external circuit so that a negligible curent flows. The emf of a cell cannot be measured with an ordinary voltmeter as the resistance is insufficient. It is usually measured with a high resistance voltmeter or a potentiometer.

XIII.10. Electrode potentials

The potential difference between a metal and a solution of its ions is dependent upon the materials used, the temperature and the concentration of the solution. The condition are standardised with the temperature 25°C and the concentration of metal ions of 1 mol dm^{-3}. The **electrode potential** E is the potential difference in volts between the metal and the solution of metal ions. The standard electrode potential (represented by E^*) is the electrode potential that exists when the solution of metal ions has a concentration of 1 mol dm^{-3} and the temperature is 25°C. The potential difference is measured relative to the standard hydrogen electrode.

The standard electrode potential E^* for some common metals are given in Table XIII.1. Do not try to remember these values, they will be given on the examination paper. Do remember that, by convention, the *reduced* form (*i.e. after* gain of electrons) is put on the *right* of the equation for which E^* is given, so that an *electropositive* metal has a *negative* E^*.

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It is not possible to measure the potential difference between a metal and its ions in solution directly. It is possible, however, to measure the potential difference between two electrodes. The hydrogen electrode is used as a standard reference electrode and its standard electrode potential is arbitrarily taken as zero.

Table XIII.1 - Standard electrode potential for some common metals

	$E^{\ominus}$/volts
$K^+ + e^- \rightarrow K$	- 292
$Na^+ + e^- \rightarrow Na$	- 2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	- 2.37
$Zn^{2+} + 2e^- \rightarrow Zn$	- 0.76
$Fe^{2+} + 2e^- \rightarrow Fe$	- 0.44
$2H^+ + 2e^- \rightarrow H_2$	0.00 standard
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$Ag^+ + e^- \rightarrow Ag$	+0.80

The standard electrode potential of a metal M is obtained by setting up two half cells, one with a rod of M dipping into a solution (concentration 1 mol dm^{-3}) of a salt of M and the other a hydrogen electrode

Note that the arrow in the circuit from the metal M to the platinum electrode is the direction of flow of electrons when the standard electrode potential is negative. If the standard electrode potential is positive the flow of electrons is in the opposite direction. Remember that the conduction in the external circuit is electronic, but in the solution and salt bridge it is ionic.

The salt bridge replaces the porous pot in example.1. It consists of an agar jelly with added potassium chloride. It allows charge to pass through it to complete the circiut, but limits diffusion of the solutions. The voltage of the cell measured with a potentiometer or a high resistance voltmeter is taken to be the electrode potential of the metal.

Although a hydrogen electrode is taken as standard, it is not easy to set up. In practice a **calomel electrode** is often used as a secondary reference electrode. It consists of mercury in contact with solid mercury(I) chloride and a solution of potassium chloride saturated with the mercury(I) salt.

XIII.11. Working out the emf of a cell

In the Daniell cell, the meximum voltage is 1.1 volts. The cell can be represented by a cell diagram. In this case it is:

$$Zn(s) \mid Zn^{2+}(aq) \;\vdots\; Cu^{2+}(aq) \mid Cu(s)$$

This means that a zinc rod is dipped into a solution of zinc ions and this solution is connected by a salt bridge to a solution of copper(II) ions with a copper rod dipping into it.

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By convention, the more negative electrode is put on the left hand side. The emf of the cell is given by:

$$E_{cell} = E_{rhs} - E_{lhs}$$ (rhs - right hand side lhs - left hand side)

In the case of the Daniell cell

$$E_{rhs} = 0.34 \text{ volts } (Cu^{2+}(aq) + 2e^- \rightarrow Cu(s))$$

$$E_{lhs} = -0.76 \text{ volts } (Zn^{2+}(aq) + 2e^- \rightarrow Zn(s))$$

$$E_{cell} = 0.34 - (-0.76) \text{ volts} = 0.34 + 0.76 = 1.10 \text{ volts}$$

(NB If you get a negative value for the emf of the cell, it probably means you have written the cell diagram the wrong way round.)

Calculate the emf of the cell with the cell diagram

$$Fe(s) \mid Fe^{2+}(aq) \;\|\; Ag^+(aq) \mid Ag(s)$$

Emf of the cell = $E_{rhs} - E_{lhs}$

Using the figures in Table XIII.1

$$\text{emf} = 0.80 - (-0.44) = +1.24 \text{ volts}$$

XIII.12 Redox potentials

The equation

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

is a reduction process since electrons are gained. The standard electrode potential (- 0.76 volts) is a measure of the relative willingness of zinc metal to be reduced or oxidised.

For copper

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s) \qquad E^* = 0.34 \text{ volts}$$

This process therefore takes place more readily for copper than for zinc. The more positive the E^* value the more readily this process takes place.

There are three types of half cell

(i) A metal dipping into a solution of its ions *e.g.* zinc dipping into a solution of zinc sulphate.

(ii) A gas in contact with an inert electrode *e.g.* hydrogen in contact with a platinum electrode in the hydrogen electrode.

(iii) An inert metal in contact with a solution containing ions in two different oxidation states *e.g.* a platinum electrode dipping into a solution containing $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ ions.

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It is possible to extend Table XIII.1 by including non metals. The standard redox potentials are measured by forming a half cell of one of the three types above and measuring the voltage with reference to the hydrogen electrode. The standard redox potentials for some non metals are given in Table XIII.2.

Table XIII.2 - Standard redox potentials for some non metals

	E^*/volts
$\frac{1}{2} I_2 + e^- \rightarrow I^-$	+0.54
$\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-$	+1.36
$\frac{1}{2} F_2 + e^- \rightarrow F^-$	+2.85

XIII.13. The electrochemical series

The arrangement of elements in order of their standard electrode potentials (Table XIII.1 and XIII.2) leads to the **electrochemical series**. The lement with the greatest negative E^* value is placed at the top of the list.

You may have met the electrochemical series at Olevel, or it may have been called the **reactivity series** although the two are not exactly the same. The electrochemical series is useful for a number of reasons. Usually we restrict it only to metals.

(i) The order of reactivity of metals decreases down the series. For non-metals the reactivity increases down the series. (Table XIII.3)

(ii) The electrochemical series can be used to predict reactions. *E.g.* if iron is added to copper(II) sulphate solution, a reaction takes place producing iron(II) sulphate and copper.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4 + Cu(s)$$

At O level it would be sufficient to state that a reaction takes place because iron is above copper in the reactivity series. At A level it would be necessary to use the E^* values.

Table XIII.3 - Order of reactivity for metals and non-metals

metals	*non-metals*	
potassium		
sodium		
Decreasing magnesium		
reactivity zinc		
iron		
copper		
silver		
	iodine	
	bromine	**Increasing**
	chlorine	**reactivity**
	fluorine	

The cell diagram is

$Fe(s) \mid Fe^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$.

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From the values in Table XIII.1, the emf of the cell is +0.78 volts (*i.e.* 0.34 - (- 0.44). In § XIII.7 it will be seen that a reaction is feasible if the E^* for cell is positive.

(iii) The electrochemical series explains why a piece of iron can be protected by galvanising, *i.e.* coating with a layer of zinc. If the surface is scratched so that water (containing dissolved carbon dioxide to produce an electrolyte) is in contact with both metals, an electrochemical cell is set up:

$$Zn(s) \mid Zn^{2+}(aq) \,\vdots\, Fe^{2+}(aq) \mid Fe(s)$$

This represents a cell with an E^* value of +0.32 volts: the corrosion of iron is the reverse and is therefore unfavourable.

(iv) The electrochemical series can predict the products of electrolysis.

(v) The electrochemical series is related to the methods available for extracting metals from metal ores.

XIII.14. The feasibility of a reaction

If a chemical reaction is to take place spontaneously, the **standard free energy change** ΔG° must be negative. There is an equation which relates ΔG° to the standard redox potential E°.

$$\Delta G^\circ = - nFE^\circ$$

where n is the number of electrons transferred and F is Faraday's constant. For a reaction to be feasible, E° should be positive.

XIII.15.What is electrode potential ?

The **electrode potential** of a metal M is represented by equation

$$M(s) \rightarrow M^{n+}(aq) + ne^-$$

NB This process is taking place in solution and the value would not be the same as the ionisation energy which takes place in the gas phase.

The change above can be considered to take place in three stages:

(i) Sublimation:

$$M(s) \rightarrow M(g)$$

Energy is required to break up the metal lattice.

(ii) Ionisation:

$$M(s) \rightarrow M^{n+}(g) + ne^-$$

Energy is required to remove n electrons from the gaseous atoms of M.

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(iii) Hydration: energy is liberated when ions are hydrated by water molecules.

Lithium and calcium have standard electrode potentials more negative than expected

$$Li^+(aq) + e \rightarrow Li(s) \qquad E^o = -3.04 \text{ volts}$$

$$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \qquad E^o = -2.87 \text{ volts}$$

Lithium and calcium occupy different places in the activity series and the electrochemical series. They have relatively high negative E^o values due to the high hydration energies of very small ions. The electrode potential is a measure of three processes - sublimation, ionisation and hydration.

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XIV. CHEMISTRY OF THE NONTRANSITION ELEMENTS

-Hydrogen and the first period-

XIV.1. Hydrogen

XIV.1.1. Introduction

The hydrogen atom has the simplest structure of all atoms. It consists of a nucleus of charge +1 with a single extranuclear electron. Three isotopes are known: ^1H, ^2H (deuterium or D) and ^3H (tritium or T). The normal form of the element is the diatomic molecule, H_2, D_2, T_2, HD, HT, DT.

Water is the most important hydrogen compound; other of great significance are hydrocarbons, carbohydrates, ammonia and its derivatives.

It is a colorless, ordorless, gas, virtually insoluble in water. It is most easily prepared by the action of dilute acids on metals such as Zn or Fe and by electrolysis of water; industrially hydrogen may be obtained by thermal creacking of hydrocarbons, by the reduction of water by carbon (water gasreaction) and in other ways.

Hydrogen is not exceptionally reactive. It burns in air to form water and will react with oxygen and the halogens explosively under certain conditions. The gas at high temperatures will reduce many oxides either to lower oxides or to the metal. At elevated temperatures in the presence of suitable catalysts, it will react with N_2 to form NH_3. With electropositive metals and most nonmetals it forms hybrids.

The dissociation of hydrogen is highly endothermic, and this accounts in part for its rather low reactivity at low temperatures:

$$H_2 = 2\ H \qquad \Delta H_o^0 = 103.2 \text{ kcal/mole}$$

Atomic hydrogen is exceedingly reactive chemically, being a strong reducing agent.

XIV. 1.2. The bonding of Hydrogen

The chemistry of hydrogen depends mainly on three electronic processes:

1. Loss of the valence electron. The 1s valence electron may be lost to give the hydrogen ion, H^+ - the proton. Its small size ($r \sim 1.5 \times 10^{-13}$cm) relative to atomic sizes ($r \sim 10^{-8}cm^{-1}$) and charge result in the proton having a unique ability to distort the electron

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clond surrounding other atoms; the proton accordingly never exists as such, except in gazeous ion beams, and is ivariably associated with other atoms or molecules in condensed phases, for exemple, at the H_3O^+ ion.

2. Acquisition of sn electron. The hydrogen atom can acquire an electron, attaining the $1s^2$ structure of He, to form the hybride ion, $H:^-$, exists essentially in the saline hydrides (e.g., KH and CaH_2), which are formed by the most electropositive metals.
3. Formation of an electron pair bond. The hydrogen atom again attains the $1s^2$ structure bz formation of an electron pair bond. This bond may be homopolar, as in H_2 molecule, but in other cases has a heteropolar nature, as, for example, in HCl.

XIV. 1.3. The Hydrogen Ion

For the reaction $H_{(g)} = H^+_{(g)} + e^-$ $\Delta H = 313$ Kcal/mole. The ionization potential is 13.595 eV.

Hydrogen can form the hydrogen ion only when its compounds are dissolved in media which solvate protons. The solvation process thus provides the energy required for bond rupture. The order of magnitude of these solvation energies can be appreciated by considering the solvation reaction in water:

$$H^+_{(g)} + x\ H_2O = H^+_{(aq)} \quad \Delta H = -268 \text{ Kcal/mole}$$

Compounds which furnish solvated hzdrogen ions in suitable solvents, such as water, are acids, or more particularly, protonic acids. Since the most important aspect of the chemistry of the hydrogen ion is tahat in aqueons media, this case will be considered in more detail. The nature of the hydrogen ion in water, which should more correctly be called the hydroxomium ion, H_3O^+, is discussed below.

Water itself is weakly ionized: $2\ H_2O = H_3O^+ + OH^-$ or

$$H_2O = H^+ + OH^-$$

Other cases of such self-ionization where one molecule solvates a proton originating from another are the following:

$$2\ H_2SO_4 = H_3SO_4^+ + HSO_4^-$$

and liquid ammonia

$$2\ NH_3 = NH_4^+ + NH_2^-$$

In aqueous solutions, the hydrogen ion concentration is often given in terms of pH, defined as $-\log_{10}[H^+]$, where $[H^+]$ is the hydrogen ion activity, which may be considered to approximate to the molar concentration of H^+ ions in very dilute solutions. At 25^0 the ionic product of water is

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$$K_W = [H^+][OH^-] = 1 \times 10^{-14}\ M^2$$

This value is significantly temperature dependent. When $[H^+]= [OH^-]$, the solution is said to be neutral and $[H^+]= 1 \times 10^{-7}M$; that is pH = 7.0. Solutions of lower pH are acid; those of higher pH, alkaline.

The standard hydrogen electrode provides the reference for all other oxidation-reduction systems. The hydrogen half-cell or hydrogen electrode is:

$$H^+_{(aq)} + e^- = 1/2\ H_2\ (g)$$

By definition, the potential of this system is zero ($E^0 = 0.000$ V) at all temperatures when an inert metallic electrode dips into a solution of hydrogen ions of unit activity (i.e. pH = 0) in equilibrium with H_2 gas at 1 atm. pressure. The potentials of all other electrodes are then referred to this defined zero.

The difficulties which are sometimes caused by the so-called electrochemical sign conventions have arisen largely because the term "electrode potentila" has been used to mean two distinct things:

(1) The potential of an actual electrode.

For example, a zinc rod in an aqueous solution of zinc ions at unit activity (a = 1) at 25^0 has a potential of -0.7627 V relative to the standard hydrogen electrode. Physically the zinc electrode is richer in electrons then the hydrogen electrode.

(2) The potential of a half reaction

Using the same chemical system as an example and remembering also that the Gibbs free energy of the standard hydrogen electrode is also defined as zero, we can write:

$$Zn + 2H^+\ (a=1) \rightarrow Zn^{2+}\ (a=1) + H_{2\,(g)}\quad \Delta G^0 = -35.18\ Kcal$$

$$Zn \rightarrow Zn^{2+}\ (a=1) + 2e^-\quad E^0 = -\Delta G^0/nF = +0.7627\ V$$

$$Zn^{2+}\ (a=1) + H_{2\,(g)} \rightarrow Zn + 2H^+\ (a=1)\quad \Delta G^0 = -35.18\ Kcal$$

$$Zn^{2+}(a=1) + 2e^- \rightarrow Zn\quad E^0 = -\Delta G^0/nF = +0.7627\ V$$

The potential of the zinc couple, defined by $\Delta G^0 = -nFE^0$ (n = number of electrons = 2, F = the Faraday) has to change sign accordingly.

The half-reaction

$$Zn \rightarrow Zn^{2+} + 2e^-$$

involves oxidation and its potential is an oxidation potential whose sign is that of the so-called American or Latimer sign convention.

The half-reaction

$$Zn^{2+} + 2e^- \rightarrow Zn^0$$

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involves reduction and its potential is a reduction potential associated with the name of the European sign convention. The reduction potential has the same sign as the potential of the actual electrode.

International Union of Pure and Applied Chemistry (IUPAC) recommended that only reduction potetials should be called electrode potentials.

Every half-reaction is therefore written in the form

$$ox + ne^- \leftrightarrow red$$

and the Nernst equation for the electrode potential, E, is

$$E = E^0 + \frac{2.3036\,RT}{nF} \log_{10} \frac{\text{activity of oxidant}}{\text{activity of reductant}}$$

E^0 is the standard electrode potential

R - the gas constant

T - the absolute temperature

XIV. 2. Hydrides and Hydride Complexes

XIV. 2.1. Saline Hydrides

The saline hydrides are white crystalline substances of generally high reactivity, best prepared by direct reaction of the metal with hydrogen gas at temperatures up to ~ 700^0. They can be dissolved in molten alkali halides and on electrolysis of such a solution, for example, CaH_2 dissolved in LiCl + KCl at 360^0, hydrogen is released at the anode. LiH alone can be melted without decomposition. The $H:^-$ and its salts react instantly and completely with any substance affording even the minutest traces of H^+, such as water, according to the reaction.

$$NaH + H^+ = Na^+ + H_2$$

The saline hydrides are excellent reducing agents

XIV. 2.2. Hydride complexes

Hydride complexes are compounds which can be regarded, as containing $H:^-$ ions coordinated to metal ions. In many cases such a description is very formal.

1. *Nontransition elements*

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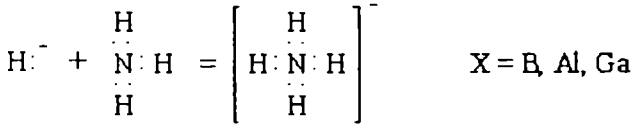
The most important hydride complexes of non-transition elements are formed by boron, aluminium, and gallium, for example, $Na[BH_4]$, $Li[GaH_4]$, $U(BH_4)_4$, $Al(BH_4)_3$. All of these XH_4^- ions are believed to be tetrahedral since this structure has been established for the BH_4^- ion.

The chemistry of these substances may be understood through consideration of a hypothetical equilibrium representing their formation.



X = B, Al, Ga

The XH_3 group behaves as an electron acceptor and the hydride ion as an electron donor. It might then be expected that the thermal and chemical stabilities of the three anions should then vary according to the Lewis acid behaviour of XH_3. This order is B > Al > Ga.

The hydrolysis of the XH_4^- ions

$$4\ H_2O + XH_4^- \rightarrow 4\ H_2 + X(OH)_3 + OH^-$$

is probably initiated by reaction of XH_4^- with H^+ to form H_2 and XH_3 the later then reacting further.

In effect, XH_3 is competing with the acceptor H^+ for the hybride ion.

Thus, sodium borohydride is quite soluble in water, undergoing only a slight initial decomposition which renders the solution basic and prevents further hydrolysis. It is, of course, completely hydrolyzed in acid, but Na salts of AlH_4^- and GaH_4^- are rapidly and often explosively hydrolyzed by water alone.

The stability and othert properties of a given XH_4^- salt depend also on the nature of the cation. While $NaBH_4$ is completely ionic, most other borohydrides and the salts of AlH_4^- and GaH_4^- show considerable covalent character. If the cation as in $Be(BH_4)_2$ or $Al(BH_4)_3$ has considerable acceptor power, it will tend to distors the XH_4^- groups, especially AlH_4^- and GaH_4^-, where the central metal is of somewhat lower acceptor ability.

Thus $Al(BH_4)_3$ is a very reactive, unstable liquid (m -64.5^0), very soluble in organic solvents.

$Be(BH_4)_2$ is a solid and is insoluble in nonopolar media.

The principal use of these complex hydrides is as reducing agents in both organic and inorganic chemistry. The most generally used materials are $LiAlH_4$ and Na(K) BH_4, which are soluble in certain ethers like diethylene glycol dimethyl ether.

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2. *Transition elements*

They are most commonly prepared by the action of BH_4^- on a halo complex though numerous other methods are used in particular cases. Some representative aomplexes are the following :

$[ReHg]^{2-}$, $[Mn(CO)_5H]$, $[Fe(CO)_4H_2]$, $[Fe(CO)_4H]^-$, $[Pt(PR_3)_2XH]$; X = Cl, Br, I, SCN

A few observations about these compounds as a class can be made here:

(a) In all cases where structural data are available, the hydrogen appears to be acting as an ordinary monoatomic, uninegative ligand, as $H:^-$.

(b) In the structural and stoichiometric senses $H:^-$ is interchangeable with ligands such as Cl^-, Br^-, I^-, SCN^-.

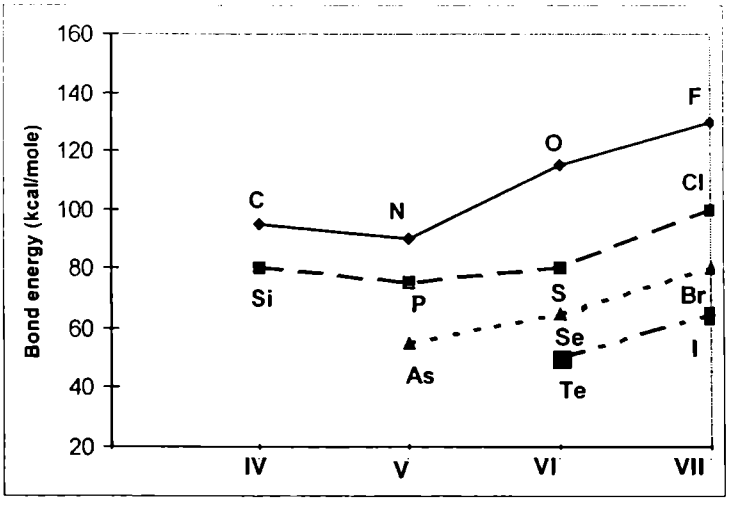
(c) The complexes exhibit M–H stretching bands in the infrared in the range 1700-2250 cm^{-1}.

(d) The hybride ion appears to lie between H_2O and NH_3 in the spectrochemical series.

XIV. 2.3. Covalent Compounds of Hydrogen

A few general remarks about covalent hydrogen compounds are pertinent here.

Except in H_2 itself, where the electronegativity difference is zero and the resonance structures $H^+ H^- \leftrightarrow H^- H^+$ are of equal weight all H–X bonds will possess some polare character. In spite of the heteropolar nature of H–X bonds, many compounds in this class are properly called covalent hydrides. The strength of H–X bonds and the thermal stability of covalent hydrides seem to depend on the electronegativities and size of the element X. The variation in bond strength in some binary hydrides is shown in Figure VIV.1.



Thermal stability, in the sense of resistence to the reaction

$$H_nX \rightarrow \frac{n}{2} H_2 + \frac{1}{x} X_x$$

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invariably decreases with increasing Z. Generally, for two elements of about eqyal electronegativity, the heavier element forms the less stable hydride. Thus the stability orders $CH_4 > H_2S$ and $PH_3 > TeH_2$.

XIV. 2.4. Other Hydrides

A rough attempt to classify the various types of hydrogen compounds, which are all loosely called "hydrides" is shown in Figure VIV.2.

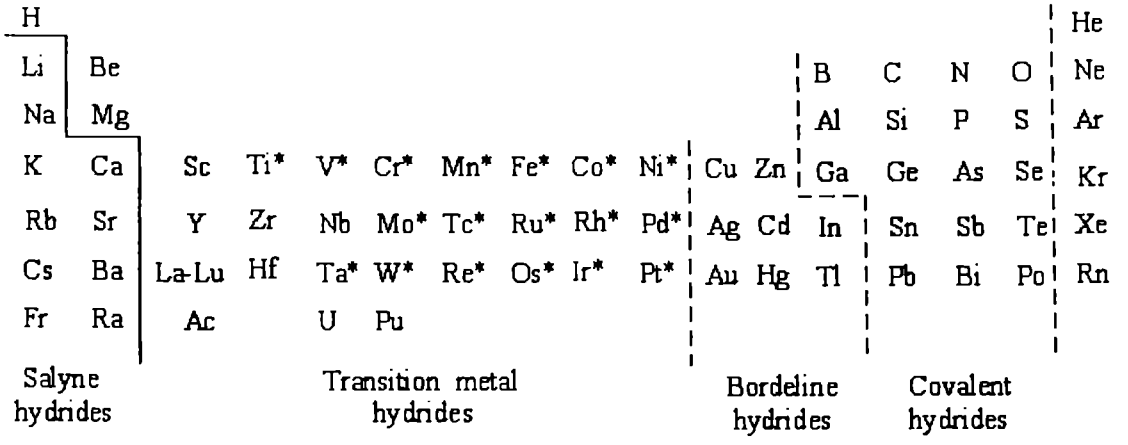
H
He
Li Be
B C N O Ne
Na Mg
Al Si P S Ar
K Ca Sc Ti* V* Cr* Mn* Fe* Co* Ni* Cu Zn Ga Ge As Se Kr
Rb Sr Y Zr Nb Mo* Tc* Ru* Rh* Pd* Ag Cd In Sn Sb Te Xe
Cs Ba La-Lu Hf Ta* W* Re* Os* Ir* Pt* Au Hg Tl Pb Bi Po Rn
Fr Ra Ac U Pu
Salyne hydrides
Transition metal hydrides
Bordeline hydrides
Covalent hydrides

Figure VIV.2- A classification of the hydrides. The starred elements are the transition elements for which complex molecules or ions containing M –H bonds are known

The hydrides of beryllium and magnesium, BeH_2 and MgH_2, seem to represent a transition between the ionic and covalent hybrides. Both are white nonvolatile solids, insoluble in organic media.

They appear to be polymerized, and it has been suggested that this is effected by hydrogen bridging similar to that in the boranes. Both react violently with water, alcohols, and both like the saline hydrides, are powerful reducing agents.

The larger group of borderline hydrides are mostly of a very uncertain nature. Copper hydride, CuH, seems to be a definite compound, but hydrides of the other elements are certainly unstable and difficult to prepare. CuH is a red-brown solid with some reducing properties, insoluble and apparently stable toward water, although decomposed by acids to liberate hydrogen.

The transition metal binary hydrides, also called metallic hydrides, are commonly grouped as a class.

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The MH_2 are grey solids which react with water and acids to produce hydrogen. They have metallic properties because there is still one unused valence electron per metal atom which may occupy electronic conduction bands in the solid. UH_3 is a stoichiometric with a rather complex structure, and is formed quite exothermically, ΔHg^0 = -30.8 Lcal/mole. UH_2 doesn't exist.

Ti, Zr and Hf absorb hydrogen exothermically, giving nonstoichiometric compounds with compositions such as $TiH_{1.7}$ and $ZrH_{1.9}$.

Pd absorb appreciable amounts of hydrogen gas, but H/Pd ratios do not exced ~ 0.7 at room temperature.

XIV. 3. The Hydrogen Bond

XIV. 3.1. Experimental Evidence

Substances containing hydrogen bond to the most electronegative elements frequently exhibit properties best explained by assuming that the hydrogen atom has a small but significant affinity for other electronegative atoms while remaining strongly bonded to the first one. This relatively weak secondary bond is called the hydrogen bond. We shall employ the following notation for a hydrogen bond between an H atom bonded initially to atom X and another atom Y which has one or more pairs of electrons:

$$X - H \ldots\ldots Y$$

The properties of the hydrogen bond are:

1. *Molecular association*

If the boiling point of the covalent hydrides are plotted aginst molecular weight as in Figure 36 it is at once abvious that the boiling points of H_2O, HF and NH_3 are out of line in a direction indicating some additional intermolecular attraction not significantly operative in the other substances. It is evident that only the hydrides of F, O and N have significant intermolecular attraction owing to the existence of strong hydrogen bonds, with Hcl showing evidence of slight deviation. All experimental evidences indicate that hydrogen bond are most important when the elements X and Y are F, O, N or Cl.

The order of magnitude of the forces with which we are dealing, namely, energies of 1-10 Kcal/mole as compared to the range 30 - 100 Kcal/mole for ordinary chemical bonds. In the carboxylic acids there are hydrogen bonds too and the acetic acid for example is a dimer shows the following configuration.

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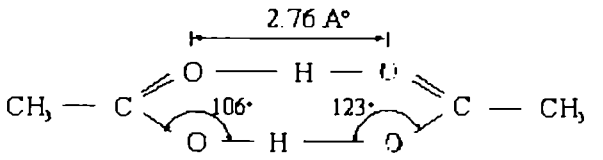

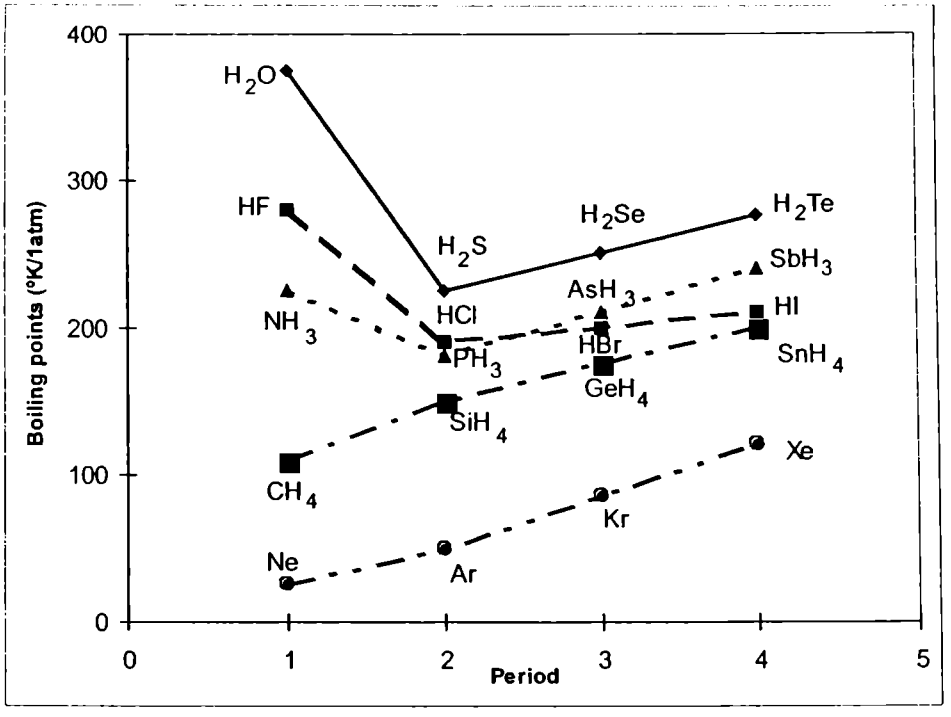

Figure VIV.3- Boiling points of some molecular hydrides

2. *Entropy data.* The structure of ice is such that each oxygen atom is surrounded tetrahedrally by four hydrogen atoms, two of which are covalently bonded to it, the other two being bonded to other oxygens but forming hydrogen bonds to the oxygen atom under consideration, as in Figure VIV.4

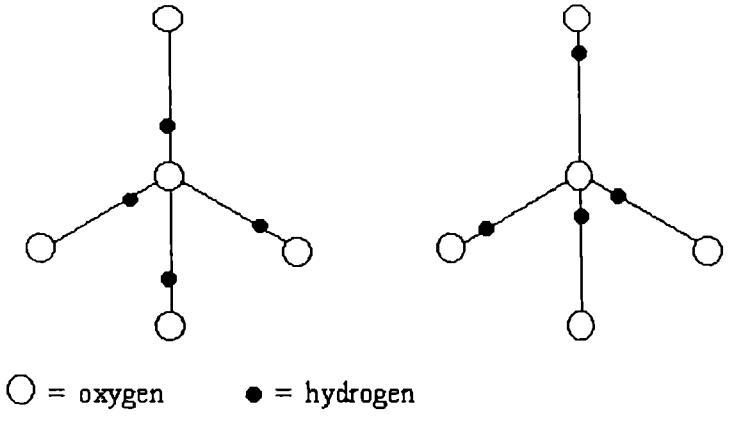

Figure VIV.4- Two possible configurations about an oxygen atom in ice

Entropy is defined, statistically, by the equation:

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$$S = - R \ln W$$

R is the gas constant; (~2.0 cal/deg); W is the probability of the state of the system.

For a symetric arrangement at 0^0K S will be zero. The value S = 0.81 ± 0.05 is obtained for ice, giving excellent confirmation of the unsymmetrical model of ice.

3. *Infrared evidence.* When the grouping X–H enters into hydrogen bond formation with the atom Y, the X–H stretching frequency (cm^{-1}) is lowred

Depression of the X–H stretching frequency shows the existence of hydrogen bonding X–H.....Y. It will be noted that the decreasing X .....Y distance both $\Delta\nu$ and the bond energy increase. For example: F– H – F; 2.26 bond length; ~ 17 Kcal/mole bond energy $\Delta\nu$ ~ 2700 cm^{-1}; N; N–H .....N (melamine) 3.00 A°; ~ 6 Kcal/mole; ~ 120 cm^{-1} respectively.

XIV. 3.2. Hydrogen

XIV.3.2.1. Introduction

- Paracelsus (1493-1541) noticed that an inflamable gas is produced when dilute acids react with certain metals.
- The English physicist, Cavendish, first isolated hydrogen and recognized it as a special gas (1766).
- The French chemist, Lavoisier, suggested the name, hydrogen, from the Greek words, *hydro* meaning water, and *genes* meaning forming.

XIV.3.2.2. Occurrence

- Only about 0.95 % by weight of the earth's crust is hydrogen.
- But 16.54 % of all the atoms of the earth's crust, including the ocean and atmosphere, are hydrogen.
- Hydrogen occurs principally in chemical combination, water (H_2O), being the most common compound.
- Combined Hydrogen.
    1. One-ninth by weight of water, H_2O.
    2. An important constituent of all animal and vegetable tissues.

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3. In chemical combination with carbon forming various hydrocarbons such as petroleum, gasoline, turpentine, rubber, and methane, CH_4.
4. In chemical combination with nitrogen, NH_3; sulfur, H_2S; and the halogens, Hcl.
5. An essential constituent of all acids as in sulfuric acid, H_2SO_4; hydrochloric acid, HCl; nitric acid, HNO_3; and acetic acid, $HC_2H_3O_2$.

- Free Hydrogen.
  1. In natural gas and volcanic gases.
  2. In coal gas and water gas.
  3. Enormous quantities in the atmosphere of the sun.
  4. Traces formed during some fermentations and decay.
  5. Only 0.01 % of the atmosphere. Perhaps greater quantities exist in the rarefied stratosphere at hights of twenty miles or more.

XIV.3.2.3. Preparation

- Laboratory Methods.
  1. By the action of non-oxidizing acids.

Zinc + sulfuric acid → hydrogen + zinc sulfate.

$$Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4$$

Aluminium + hydrochloric acid → hydrogen + aluminium chloride.

$$2\ Al + 6\ HCl \rightarrow 3\ H_2 + 2\ AlCl_3$$

  2. By the interaction of metals with water.

Sodium + water → hydrogen + sodium hydroxide.

$$2\ Na + 2\ H_2O \rightarrow H_2 + 2\ NaOH$$

Calcium + water → hydrogen + calcium hydroxide.

$$Ca + 2\ H_2O \rightarrow H_2 + Ca(OH)_2$$

  3. By the interaction of metals with alkali bases.

Zinc + sodium hydroxide + water → hydrogen + ?.

$$Zn + 2\ NaOH + 2\ H_2O \rightarrow H_2 + Na_2[Zn(OH)_4]$$

Aluminium + sodium hydroxide + water → hydrogen + ?.

$$Al + NaOH + 3\ H_2O \rightarrow H_2 + Na[Al(OH)_4]$$

Silicon + sodium hydroxide + water → hydrogen + sodium silicate?.

$$Si + 2\ NaOH + H_2O \rightarrow 2\ H_2 + Na_2SiO_3$$

  4. By decomposing metallic ?.

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Zinc + sodium hydroxide + water → hydrogen + ?.

$$Zn + 2\ NaOH + 2\ H_2O \rightarrow H_2 + Na_2[Zn(OH)_4]$$

- Commercial Methods.

1. By the reduction of water with hot carbon, known as the water gas reaction.

Heated coke + steam $\xrightarrow{\Delta}$ hydrogen + carbon monoxide

$$C + H_2O \xrightarrow{\Delta} H_2 + CO$$

2. By decomposing water by electrolysis, in the presence of dilute sulfuric acid or sodium hydroxide.

Water → hydrogen + oxygen.

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

3. By the interaction of steam and heated iron.

Steam + iron $\xrightarrow{\Delta}$ hydrogen + magnetic iron oxide

$$4\ H_2O + 3\ Fe \xrightarrow{\Delta} 4\ H_2 + Fe_3O_4$$

4. By the interaction of certain metals or silicon and water in the presence of sodium hydroxide.

Zinc + water $\xrightarrow{\Delta}$ hydrogen + zinc hydroxide

$$Zn + 2\ H_2O \xrightarrow{\Delta} H_2 + Zn(OH)_2$$

Silicon + water $\xrightarrow{\Delta}$ hydrogen + silicon hydroxide

$$Si + 4\ H_2O \xrightarrow{\Delta} 2\ H_2 + Si(OH)_4$$

5. Large quantities of hydrogen are obtained as a byproduct in the manufacture of sodium hydroxide by the electrolysis of salt brine, NaCl.

Sodium chloride + water $\xrightarrow{\Delta}$ hydrogen + chlorine + sodium hydroxide

$$2\ NaCl + 2\ H_2O \xrightarrow{\Delta} H_2 + Cl_2 + 2\ NaOH$$

6. By the destructive distillation of coal. The methane, CH_4, produced may be removed by liquefaction.

XIV.3.2.4. Physical Properties

- Hydrogen is a colorless, odorless and tasteless gas.
- Atomic weight, 1.008. Atomic number, 1.
- Critical temperature, -234.5°C. Critical pressure, 20 atmosphere.
- Boiling point, -252.8°C.
- Freezing point, -259°C, as a snow white solid.

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- Lightest of all gases. (1 liter weighs 0.08985 g.) 1/14 as heavy as air and 1/16 as heavy as oxygen.
- 1.8 cc dissolves in 100 ml of water at 25°C, and 760 mm pressure.
- Hydrogen is readily absorbed by finely divided metals, such as palladium, platinum and nickel.
    1. One volume of palladium absorbs 900 volumes of hydrogen.

XIV.3.2.5. Chemical Properties

- Valence, 1, usually positive.
- Hydrogen combines readily with oxygen to form water.

$$\text{Hydrogen + oxygen} \rightarrow \text{water}$$

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

- Hydrogen combines with active metals such as lithium, sodium, calcium, and barium to form hydrides.

$$\text{Sodium + hydrogen} \xrightarrow{\Delta} \text{sodium hydryde}$$

$$2\ Na + H_2 \xrightarrow{\Delta} 2\ NaH$$

- Hydrogen combines with many non-metals.

$$\text{Hydrogen + chlorine} \rightarrow \text{hydrogen chloride}$$

$$H_2 + Cl_2 \rightarrow 2\ HCl$$

$$\text{Hydrogen + sulfur} \xrightarrow{\Delta} \text{hydrogen sulfide}$$

$$H_2 + S \xrightarrow{\Delta} H_2S$$

$$\text{Hydrogen + nitrogen} \rightarrow \text{ammonia}$$

$$3\ H_2 + N_2 \rightarrow 2\ NH_3$$

- Hydrogen is an active reducing agent.

$$\text{Copper oxide + hydrogen} \xrightarrow{\Delta} \text{copper + water}$$

$$CuO + H_2 \xrightarrow{\Delta} Cu + H_2O$$

XIV.3.2.6. Uses

- *Cutting and welding metals.* The oxy-hydrogen flame produces temperatures of approximately 2,500°C. The atomic hydrogen torch, developed about 1926, forces the hydrogen through a very hot electric arc producing temperatures of 4,000 to 5,000°C.

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- *Synhetic ammonia* is produced by the direct combination of hydrogen and nitrogen under high pressures and in the presence of catalysts.
- *Balloons and dirigibles*. Hydrogen has the greatest lifting power of all gases. because of its flammability it is being largely displaced with helium.
- *Reducing agent*. Hydrogen is frequently used within furnaces for annealing or deoxidizing brass and metals.
- *Hardening fats*. Cottonseed, cocoanut, fish, whale and other vegetable and animal oils combine with hydrogen in the presence of finely divided nickel to form semi-solid fats. Lard substitutes and soap stock are prepared in this manner.
- *Synthetic methanol and formaldehyde*. Both methanol, often called wood alcohol, and formaldehyde are now produced commercially in large quantities from hydrogen and carbon monoxide in the presence of catalyst consisting of zinc oxide and finely divided copper.
- *Gasoline substitutes*. Motor fuels have been prepared, chiefly in Europe, by treating coal or petroleum with hydrogen at moderate temperatures under very high pressures.
- *Cooling electric generators*. Hydrogen has a greater heat conductivity than any other gas. Hydrogen circulated through the field coils and armatures has a beneficial cooling and reducing effect.
- *The hydrogen bomb*. Hydrogen has been suggested as a possible source of enormous energy by processes of nuclear fusion.

XIV.3.2.7. Analytical Test

- Hydrogen gas is readily combustible producing steam which condenses on coal objects.
- Quantitatively, hydrogen is determined by passing the gas over hot copper oxide and absorbing the water in a weighed tube of calcium chloride or other drying agent.

XIV.3.2.8. Recent Developments

- *Isotopes of hydrogen*. In 1932, Urey announced that not all atoms of hydrogen are of relative weight 1.008 (protium) but that about 1 atom in 5,000 has a relative weight of 2, known as *deuterium*, D, or H^2. In 1934, a third isotope, *tritium*, present to the extent of

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about 1 atom in 1,000,000,000, and with an atomic weight of 3 was discovered. Combinations of the heavy isotopes of hydrogen with oxygen are known as *heavy water*.

- *Ortho- and para-hydrogen.* In 1929, a German chemist, Bonhöffer, discovered that ordinary hydrogen gas consists of 25 % *ortho-hydrogen* and 75 % *para-hydrogen*. The essential difference is that the two atoms that form the molecule possess nuclei that spin in the same or opposite directions.

XIV.3.2.9. Definitions

- An *acid* contains hydrogen which can be replaced by a metal, furnishes hydrogen ions in solution, and turns litmus red.
- *Destructive distillation* involves the heating and simultaneous decomposition of organic compounds in closed retorts without the presence of air.
- *Electrlysis* involves the decomposition of a compound due to the application of electrical energy.
- An *hydride* is a compound resulting from the combination of hydrogen with another element, either metal or non-metal.
- *Hydrogenation* is the direct addition of hydrogen to a compound, usually in the presence of a catalyst.
- *Reduction* is the opposite of oxidation, or may involve the removal of oxygen. Fundamentally certain valence changes are involved due to the gain of electrons.

XIV.3.2.10. Chemical activity

- Not all metals react with all acids to produce hydrogen. Some combinations fail to react at all and other combinations produce other gaseous products. A convenient guide to what happens is found in the *Activity Series* of the metals. This is a list of the common metals arranged in the order of decreasing activity under comparable conditions. The following applications are worthy of note.
  1. Metals near the top of the series (K, Na) react violently with water, liberating hydrogen. Those somewhat lower (Mg, Al, Fe) react slowly.

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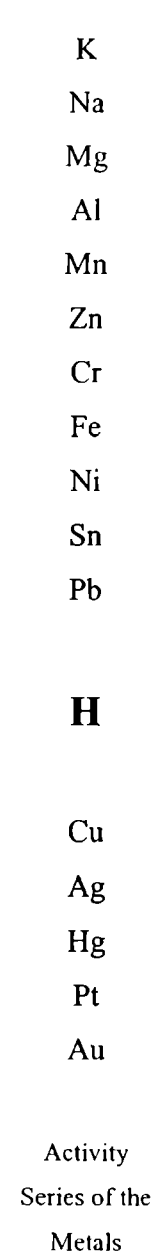

2. All metals above hydrogen react with non-oxidizing acids liberating hydrogen and forming salts. Those near the top of the series (K, Na) react violently.
3. Metals below hydrogen (Cu, Ag, Au) in the series do not react with non-oxidizing acids or hot water.
4. Acids differ greatly in their chemical activity toward these metals.
5. Nitric and concentrated sulfuric acids react with all the metals except gold and platinum, but do not ordinarily produce hydrogen but other gaseous products.
6. Metals near the top of the series (K, Mg, Mn, Fe) are seldom found free in nature; those near the bottom (Pt, Au) are usually found free in nature; and those between (Pb, Cu, Ag) are frequently found both free and in combination.
7 Those metals near the top are easily oxidized and form stable oxides; the oxides of those metals near the bottom are less easily formed and can usually be decomposed by heat.
8. Hydrogen and carbon fail to reduce the oxides of those metals near the top of the series, but readily reduce those near the bottom of the series.
9. Any metal in the series will replace any metal below it from solutions of salts of the lower metal. The farther the two metals are separated in the series the more rapid will be the replacement and the greater will be the amount of heat liberated.

\

XIV.4. The elements of the first short period

The seven elements Li, Be, B, C, N, O, F, are often referred to as the elements of the first short period of the periodic table. They constitute the first members of the groups of

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elements in the table. These elements have some properties in common with heavier elements of their respective groups (*e.g.* the outer electronic structures of gaseous atoms N $2s^2 2p^3$; P $3s^2 3p^3$), but they show highly individual behavior in many important respects (for example the normal state of nitrogen is as gaseous N_2 molecules, whereas P, As, Sb form tetraatomic molecules, such as P_4 and are solid at room temperature).

The range of chemical properties can be briefly indicated as follows:

Lithium is low-melting, highly electropositive metal, and its chemistry is maimy that of the Li^+ ion in the solid state and in solution.

Beryllium is also metallic, but is less electropositive and reactive than Li; the discrete Be^{2+} ion deos not exist in solution or lattices even in BeF_2 or BeO, there being a great tendency for Be to form at least partially covalent bonds.

Boron is essentially nonmetallic in the elemental state; it does not form simple B^{3+} cations, and its compounds contain predominantly covalent bonds. It has an extensive chemistry in combination with oxygen (borates) and with carbon in oyanoboron compounds and forms a unique series of hybrides.

Carbon is completely nonmetallic. Its chemistry is dominated by the formation of four covalent bonds, by formation of carbon-carbon bond (catenation), and by ready formation of multiple bonds to itself, nitrogen.

Nitrogen exists normally as the diatomic gas N_2, which is very unreactive because of the great strength of the N≡N triple bond. Its compounds are covalent, usually insolving three single bonds, although multiple bonds also occur. Under special circumstances the nitride ion N^{3-}, can exist.

Oxygen normally exists as a paramagnetic, diatomic gas. It forms well-defined oxide ions, O^{2-}, in many crystals and OH^- ions in crystals and in solution. Oxides may also be covalent, for example, SO_3.

Fluorine is a diatomic gas and it is extremely reactive. It forms both ionic compounds containing $F:^-$ ions and covalent compounds X–F bonds; owing to the high electronegativity of fluorine, these bonds generally have considerable ionic character.

XIV.4.1 Formation of electron pair bonds

Single bonds

All elements of the first short period have only four orbitals energetically suitable for bond formation, and can be surrounded by no more than light electrons in the valence shell.

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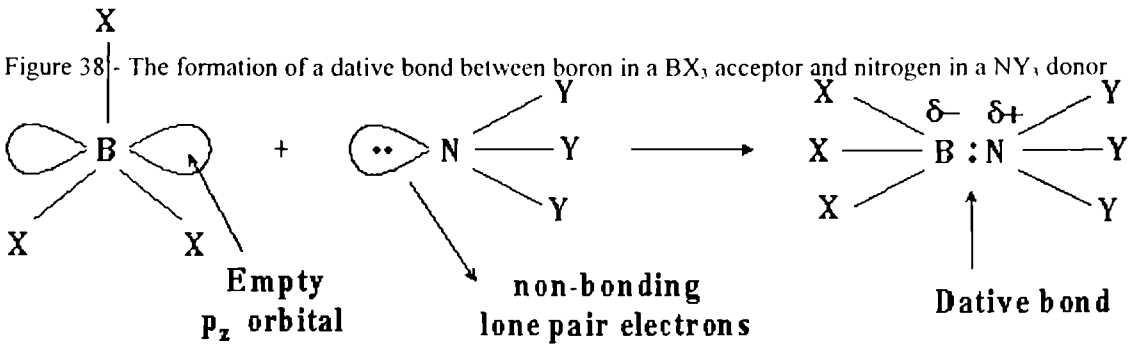

Figure 38 - The formation of a dative bond between boron in a BX_3 acceptor and nitrogen in a NY_3 donor

Thus by electron sharing, these elements can exhibit valences of only 1, 2, 3 and 4 respectively (F, O, N, C).

The atoms with four energetically useful orbitals and fewer have a strong drive to use their unoccupied orbitals. Also, atoms with too many electrons have a tendency to utilize these electrons. Thus compounds of boron, such as BCl_3, BF_3 and $B(CH_3)_3$, readily form adducts with nitrogen compounds as NH_3, $N(CH_3)_3$ etc. as illustrated in Figure 38.

The atoms as nitrogen, oxygen, fluorine possess the pairs of non-bonding electrons and can function as donors. Beryllium can form two dative bonds and lithium loses the two $2s^2$ electrons and forms a cation Li^{2+} with the hellium structure.

The number of atoms surrounding a given atom, X, is called the coordination number of X. The maximum coordination number of the first row elements is four. Beryllium and Boron frequently attain this number by functioning as an acceptor (*e.g.* $[Be(H_2O)_4]^{2+}$) and other as nitrogen atom functions as a donor atom.

The C.N = 4 is frequently for the atoms as B, C, N and more difficult for the atoms as Be, O, F.

Multiple Bonds

The elemnets C, N, and O characteristically form multiple bonds with themselves and with one another. Their congeners form anly to a minor degree P = O, S = C and S = O.

We have seen that a multiple bond can be viewed, in MO theory, as a σ bond plus one or two π bonds. The reasons why Si, P and S do not characteristically form double bonds, in contrast to C, N and O, have not been fully elucidated.

The most probable reason is that in order to approach alosely enough to get good overlap of **pπ** atomic orbitals, the heavier atoms would encounter large repulsive forces due to overlapping of their filled inner shells, whereas the small inner shall of the first row elements (*i.e.* just 1 s^2) does not produce this repulsion.

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Multiple bond formation an important feature of the elements of the first short period but not, significantly, of their congeners.

XIV.4.2. Lithium

Occurance, Isolation and Properties

The most important lithium minerals are lepidolite $Li_2(F, OH)_2Al_2(SiO_3)_3$ and spoumene $LiAl(SiO_3)_2$.

The high standard potential

$$Li^+(aq)/Li \quad E^0 = -3.045 \text{ V}$$

the metal cannot be made by electrolysis of aqueous solutions of lithium salts; this produces the hydroxide.

The metal can be obtained by electrolysis of a fused salt, usually LiCl, or by electrolysis of LiCl in pyridine, ethanol or acetone.

Freshly cut surfaces turnish in air owing to oxide and nitride formation, but the reaction with water is not so vigorous as to inflame the hydrogen.

The metal is relatively light, it has the highest melting and boiling points, 179° and 1317°.

Like other electropositive metals, lithium dissolves in liquid ammonia and various amines (*e.g.* ethylamine) to give blue solutions which conduct electricity. Lithium in ethylamine is powerful reducing agent used in organic chemistry.

The reactions of lithium metal are summarized below:

Ionic Salts; the Hydrated Li^+ Ion

Reagent	*Products*
H_2O / slow at 25°C	$LiOH, H_2$
O_2 / 100°C	Li_2O
H_2 / 700 - 800°C	LiH
N_2 / 25 - 200°C	Li_3N
NH_3 (*l*)	$LiNH_2, H_2$
Alcohols	Alkoxides, $ROLi, H_2$
Non metals, heating	Li_2C_2, Li_2S, Li_3P, etc.

Salts with common anions such as Cl^-, SO_4^{2-} are highly ionic under all conditions. The fused salts conduct electricity. Owing to its small size, the Li^+ ion has a large hydration energy, and it is often hydrated in its solid salts when the same salts of other alkalies are unhydrated, viz. $LiClO_4 \cdot 3H_2O$.

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The lithium salts of strong acids are usually the most soluble in water, and the salts of weak acids are usually less soluble than those of the other alkalics.

The vapors of the halides contain polymeric species, mainly dimers and trimers; $(LiF)_2$ and $(LiF)_3$; $(LiCl)_2$.

LiOH absorbs CO_2 to form Li_2CO_3. Since LiOH is a strong base, lithium salts of weak acids (Li_2CO_3, Li_2S) are hydrolized in solution and give pH's >7. LiOH is less soluble than NaOH.

XIV.4.3. Beryllium

General Remarks

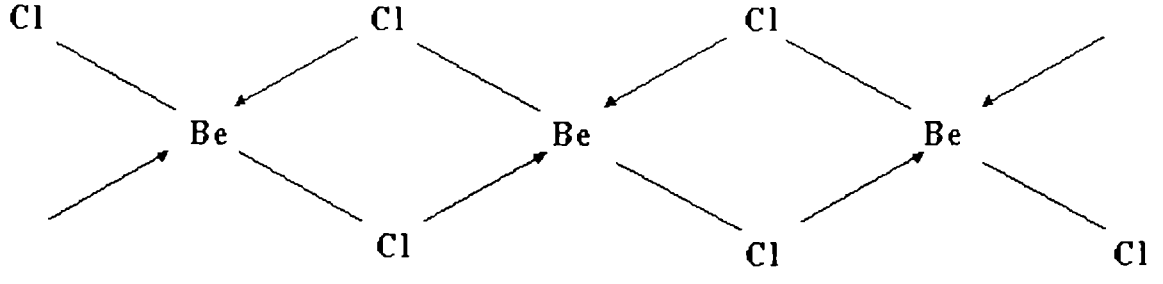
The electron configuration of the gaseous beryllium atom is $1s^2\ 2s^2$. The increased nuclear charge over that in lithium, coupled with the fact that 2s electrons only partially shield one another, has two effects.

(i) The beryllium atom has a metallic radius of only 0.89 A°, much smaller than metallic Li's 1.22 A°

(ii) The ionization potentials of Be 9.32 and 18.21 eV, are much higher than that of Li (5.39 eV), making Be for less electropositive in all its chemical behavior than Li. In fact, there are no crystalline compounds or solutions in which Be^{2+} ions exist as such. The compounds with the most electronegative elements, such as BeO and BeF_2 have at least partial covalent bonding.

To allow the formation of two covalent bonds — Be —, the Be atom is promoted to a state in which the two valence electrons occupy two equivalent sp hybrid orbitals and X — Be — X system is linear. Maximum coordination number is achieved in several ways:

1°. Polymerization may occur through bridging as in solid $BeCl_2$.



2°. By functioning as acceptors, many beryllium compounds attain maximum coordination of the metal atom. Thus the complex ions such as BeF_4^{2-} and $[Be(H_2O)_4]^{2+}$ exist.

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It may be noted that Be gives compounds often isomorphous with oxygen compounds of silicon; thus BeF_2 with SiO_2; $BaBeF_4$ with $BaSiO_4$; $NaBeF_3$ with $CaSiO_3$.

Resemblances between Beryllium and Aluminium

The similarities do in fact exist and these are the best example of the "diagonal relationship".

1°. Metallic Be, like Al, is rather resistant to acids. Thus although the potential

$$Be^{2+}(aq) / Be \qquad E^0_{calc} = -1.85 \text{ V}$$

would indicate rapid reaction with dilute acids, the rate of attack depends greatly also on the source and fabrication of the metal.

For very pure metal the relative dissolution rates are $HF > H_2SO_4 \sim HCl > HNO_3$. The metal dissolves rapidly in 3M H_2SO_4 and 5M NH_4F, but very slowly in HNO_3 because the formation of an iner oxide film on the surface.

2°. Be dissolves in strong bases to give what is called the "beryllate" ion:

$$Be + 2OH^- = Be\ O_2^{2-} + H_2$$

Al gives "aluminate" ions AlO_2^-.

Neither of these formulas for the ions is representative of the true species, which are probably four and six coordinated, respectively.

Both Be and Al oxides and hydroxides are amphoteric dissolving readily in sodium hydroxide solutions.

3°. BeO and Al_2O_3 have high melting points. BeO is polymorphic and converts into a second forme above ~ 800°C. This high temperature form is virtually isoluble in aqueous acids or bases and is only difficulty soluble in fused salts such as $KHSO_4$ or KOH. The low temperature form of BeO has wurtzite structure whereas the other alkaline earth oxides all have the NaCl structure.

The Element (Be)

Occurance, Isolation and Properties

The most important beryllium mineral is beryl, $Be_3Al_2(SiO_3)_6$.

Beryllium, like lithium is made by electrolysis of the fused chloride, but the extraction from ores is complicated. Since $BeCl_2$ is covalent has a very low electrical conductivity and NaCl is added to the melt.

The grey metal is rather light (1.86 g/cm^3) and quite hard and brittle. It is also added as an antioxidant to copper and phosphor bronzes.

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Beryllium has a much lower chemical reactivity than lithium. Some of these reactions are given in Figure 39.

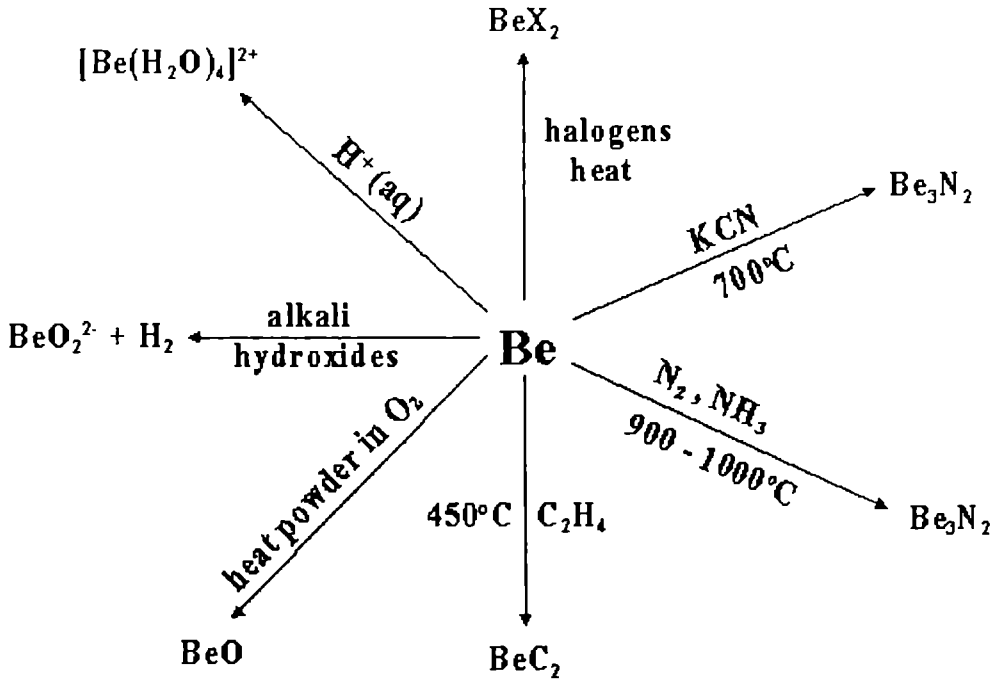

Figure VIV.6 - Some reactions of beryllium

Halides, Oxo Salts and Binary Compounds of Beryllium

⇒ **BeF_2**: is obtained as a glassy hygroscopic mass by heating $(NH_4)_2BeF_4$. The melt is a poor conductor of electricity. It is a glassy in form like silica having randomly oriented chains of F_2BeF_2Be... with F bridges. It is readily soluble in water.

⇒ **BeF_4^{2-}**:Fluoroberyllates can be made by dissloving BeO in concentrated solution of HF. . BeF_4^{2-} is tetrahedral. This ion has a crystal chemistry much like that of SO_4^{2-} and corresponding salts, for example $PbSO_4$ and $PbBeF_4$, ussually have similar structures and solubilities.

⇒ **$BeCl_2$**: is prepared by passing CCl_4 over BeO at 800°C. It dissolves in water very exothermically, and a hydrates, $[Be(H_2O)_4]Cl_2$ can be crystallized from HCl solutions of the salt. The Na_2BeCl_4 exists only in the system NaCl - $BeCl_2$ but $BeCl_4^{2-}$ is rather unstable and does not exist in solution. Salts of oxo acids are known. $[Be(H_2O)_4]SO_4$ can be dehydrated at 400°C to $BeSO_4$, which is very stable and does not decompose below 580°C. The nitrate $[Be(H_2O)_4](NO_3)_2$ melt in its own water at 60.5°C.

⇒ **BeS**: The sufide has the zinc blende structure and is insoluble in water (although all other alkine earth sulfides and Al_2S_3 are rapidly hydrolyzed by water);

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⇒ **Be_3N_2**: a white crystalline powder or colorless crystals hydrolyzed by water;

⇒ **$BeCO_3$**: is unstable and can be kept only in an atmosphere of CO_2.

⇒ **BeH_2**: not obtainable by direct reaction, may be made by action of $LiAlH_4$ on $(CH_3)_2Be$, or by thermal decomposition of $[(CH_3)_3C]_2Be$. The general properties of BeH_2 suggest that it is polymeric with hydrogen bridging.

Aqueous Chemistry of Beryllium

In concentrated acid solutions beryllium appears to exist as $[Be(H_2O)_4]^{2+}$ ions, and these occur in several salts. The solutions of beryllium salts can dissolve considerable amounts of beryllium oxide or hydroxide because beryllium readily forms oxo and hydroxo complexes with Be — O — Be and Be — OH — Be bridges.

In the precipitation of $Be(OH)_2$ some interesting effects have been observed.

If the **n** is the number of OH^- ions added per Be^{2+} ion, solutions remain clear up to **n** = 1. When **n** > 1, preicpitation commences. With halide solutions precipitation is complete at **n** = 2, but with other ions precipitation is complete at **n** = 1.8 - 1.9 indicating that such precipitates of beryllium "hydroxide" contain SO_4^{2-} , NO_3^- or ClO_4^- ions.

For **n** >1 there are $[Be(OH)^+]$ species which are soluble. There isn't $[Be(OH)]_2^{2+}$ or $[Be(OH)_4]_4^{4+}$ species.

XIV.4.4. Boron

General Remarks

The first ionization potential of boron 8.296 eV is rather high and the total energy required to produce B^{3+} ions is higher. Consequently, simple electron loss to form a cation plays no part in boron chemistry.

Instead, covalent bond formation is of major importance. Despite $2s^2\ 2p^1$ electronic structure, boron is always trivalent and never monovalent.

This is because the total energy released in formation of three bonds in a BX_3 compound exceeds the energy of formation of one bond in a BX compound by more than enough to provide for promotion of boron to a hydralized valence state of the sp^2 type. The factors appears to be responsible for the shortness of the bonds B — F, B — Cl, B — Br are the folowing:

1°. Formation of **pπ - pπ** bonds using filled **pπ** orbitals of the halogens and the vacant **pπ** orbital of boron. This is most important in BF_3.

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2°. Ionic - covalent resonance. Even in BF_3 complexes such as $(CH_3)_3N^+B^-F_3$, and BF_4^-, where the **pπ - pπ** bond must be largely or totally absent, the B — F bonds are still shortened, because of the large electronegativity difference.

3°. It is possible that because of the incomplete octet in boron, repulsions between nonbonding electrons are somewhat less than normal permitting closer approach of the bonded atoms.

Acceptor. Behavior

In BX_3 compounds the boron octet is incomplete. Aluminium makes up this insufficiency of electrons by forming dimers. The size factor may be important for BCl_3 and BBr_3, since the small boron atom may be unable as Cl and Br. The BCl_4^- and BBr_4^- ions are stable only in crystalline salts of large cations such as Cs^+ or $(CH_3)_4N^+$, but BF_4^- is quite stable.

An important consequence of the incomplete octet in BX_3 compounds is their ability to behave as acceptors (Lewis acids) and form 1:1 complexes with Lewis Bases (amines, phorphines, ethers, sulphides). The relative strenghts of the boron halides as Lewis acids are in the order

$$BBr_3 >> BCl_3 > BF_3$$

This order can be explained, in terms of boron - halogen π bonding. In an addition compound this π bonding is largely or completely lost. Calculations indicate that the π bonding energies of the trihalides are in the order

$$BF_3 >> BCl_3 > BBr_3$$

and the strength of the donor - boron bond increases in the order

$$BF_3 < BCl_3 < BBr_3$$

No satisfactory explanation has been given for this.

Comparison with Silicon and Aluminium

Elemental boron has properties which place it on the borderline between metals and nonmetals. It is a semiconductor, not a metallic conductor. Chemically, boron must be classed as a nonmetal, and in general its chemistry resembles that of silicon much more closely than that of aluminium or its other congeners Ga, In and Tl. The main resemblences to Si and differences from Al are the following:

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1°. The similarity and complexity of the boric and silicic acids is notable. Boric acid, $B(OH)_3$, is weak but definitely an acid. It has no amphoteric properties, whereas $Al(OH)_3$ is mainly basic with some amphoteric behavior.

2°. The hydrides of B and Si are volatile, spontaneously inflammable, and readily hydrolized, whereas the only binary hydrides of Al is a solid, polymeric material of uncertain structure. However, structurally, the boron hydrides are unique, having unusual stoichiometries and configurations and unusual bonding because of their *electron-deficient* nature.

3°. The redy hydrolysis of the boron halides (not BF_3) gives $B(OH)_3$, just as the silicon halides readily hydrolyze to silicic acid. The aluminium halides are only partially hydrolyzed in water.

4°. B_2O_3 and SiO_2 are similar in their acidic nature, as evidenced by their facility in dissolving metallic oxides to form borates and silicates, and both readily form glasses which are difficult to crystallize. Certain oxo salts of B and Si are structurally similar, specifically the linear $(BO_2)_x$ and $(SiO_3)_x$ ions in metaborates and pyroxene silicates, respectively.

5°. However, despite dimerization of the halides of Al and Ga and of the alkys of Al, they behave as acceptors and form adducts similar to those given by boron halides and alkyls, for example, $Cl_3Al^-N^+(CH_3)_3$. Aluminium, like boron, also forms volatile alkoxides such as $Al(OC_2H_5)_3$, which are similar to borate esters, $B(OR)_3$.

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XV. CHEMISTRY OF THE NONTRANSITION ELEMENTS

-The metals-

XV.1 The metals

Definition

- A substance possesing so-called metallic properties, such as luster, electrical and thermal conductivity, ductility, and malleability.
- Elements that furnish simple cations when their compounds are dissolved in water.
- Elements whose oxides and hydroxides are basic.
- The outer electrons of metals possess a high degree of freedom, and are readily surrendered to other elements or groups during reactions.

Occurrence

- Free or native. For example, Au, Pt, Ag, and Cu.
- Oxides. For example, Hematite, Fe_2O_3; bauxite, Al_2O_3; zincite, ZnO; and cuprite, Cu_2O.
- Sulfides. For example, Galena, PbS; cinnabar, HgS; argentite, Ag_2S; sphalerite, ZnS; and chalcopyrite, $CuFeS_2$.
- Carbonates. For example, Siderite, $FeCO_3$; smithsonite, $ZnCO_3$; malachite, $CuCO_3 - Cu(OH)_2$; cerussite, $PbCO_3$; limestone, $CaCO_3$; and dolomite, $MgCO_3 - CaCO_3$.
- Sulfates. For example, Barytes, $BaSO_4$; and anglesite, $PbSO_4$.
- Silicates. For example, Willemite, Zn_2SiO_4.
- Miscellaneous. For example, Sylvanite, $AgAuTe_2$; and horn silver, AgCl.

Physical Properties

- Luster.
  1. Most metals are a shiny white to gray in appearance.
  2. Gold is yellow, and copper is reddish.
- Hardness.
  1. Many alloys of metals are harder than pure metal.
  2. Chromium, because of its harness, wears well on plated articles.
  3. The alkali metals are waxy and soft.

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- Malleability.
  1. This is the ability of a metal to be rolled or hammered into thin sheets.
  2. One once of gold may be hammered out so as to cover 160 square feet. Gold leaf is about $\frac{1}{300,000}$ of an inch thick.
- Ductility.
  1. This is the ability of a metal to be drawn into wire.
  2. One grain of gold may be drawn into a wire 500 feet long.
- Tenacity or strength.
  1. Lithium, the lightest metal, wieghs only 53 g per cc., and readily floats on water.
  2. A cubic centimeter of osmium weighs 22.5 grams.
- Heat conductivity.
  1. Silver, gold, copper, and aluminium have high thermal conductivity.
- Electrical conductivity.
  1. Pure metals are better conductors of electricity than alloys.
  2. Silver, copper, gold, and aluminium have high electrical conductivity.

Chemical Properties

- Metals are electropositive in character and tend to lose electrons during reactions.

$$Zn \rightarrow Zn^{++} + 2e$$

- Metals combine directly with oxygen, sulfur, and the halogens.

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

$$Zn + S \rightarrow ZnS$$

$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

- Metals produce cations, which are attracted to the cathode, when their salts are dissolved in water.

$$NaCl \leftrightarrow Na^{+} + Cl^{-}$$

$$Cu(NO_3)_2 \leftrightarrow Cu^{++} + 2\ NO_3^{-}$$

- Active metals replace less active metals from their solutions.

$$Fe + CuSO_4 \rightarrow CuSO_4 + Cu$$

$$Cu + Hg(NO_3)_2 \rightarrow Cu(NO_3)_2 + Hg$$

- Metals do not dissolve except by chemical reaction.

$$2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2 \uparrow$$

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow$$

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- Metals react with acids in two ways, depending upon the nature of the acid and activity of the metal.

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2 \uparrow$$

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + H_2O + 2\ NO \uparrow$$

- Active metals react with bases.

$$2\ Al + 6\ NaOH \rightarrow 2\ Na_3AlO_3 + 3\ H_2 \uparrow$$

XV.1.1. Metallurgy

Fundamental Operations Usually Involved

- Concentration.
  1. Metals found native need only be concentrated for use.
  2. Gold is concentrated by amalgamation and the cyanide process.
  3. Concentrated deposits of ores are generally utilized.
  4. Other ores are concentrated by sifting, magnetism, froth-flotation, etc.
- Oxidation.
  1. Oxide ores as, Fe_2O_3, require no further oxidation.
  2. Zinc sulfide and lead sulfide are oxidized before reduction.

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2 \uparrow$$

$$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2 \uparrow$$

- Reduction.
  1. Carbon is the most common reducing agent.

$$Fe_2O_3 + 3\ C \xrightarrow{\Delta} 2\ Fe + 3\ CO \uparrow$$

  2. Metallic aluminium is sometimes used. (Goldshmidt process).

$$Cr_2O_3 + 2\ Al \rightarrow 2\ Cr + Al_2O_3$$

$$Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe$$

  3. Metallic magnesium is sometimes used.

$$B_2O_3 + 3\ Mg \rightarrow 3\ MgO + 2\ B$$

$$SiO_2 + 2\ Mg \rightarrow 2\ MgO + Si$$

  4. Hydrogen is occasionally used.

$$CuO + H_2 \rightarrow Cu + H_2O$$

  5. Sodium is occasionaly used.

$$TiCl_4 + 4\ Na \rightarrow Ti + 4\ NaCl$$

$$SiCl_4 + 4\ Na \rightarrow Si + 4\ NaCl$$

  6. Reduction by heat.

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$$2\ HgO \rightarrow 2\ Hg + O_2$$

7. Metallic iron is occasionally used.

$$Sb_2S_3 + 3\ Fe \rightarrow 3\ Sb + 3\ FeS$$

- Purification.

  1. A flux is frequently added to combine with objectionable impurities forming a slag, *e.g.*, limestone is frequently added to iron ore in the blast furnace.

  2. Impurities may be removed by oxidation. For example, sulfur and phosphorous are removed from iron by oxidation in the Bessemer converter.

  3. Electrolysis. For example, copper is eventually purified by electrolysis.

- Electrolytic methods.

  1. Finding increased use in recent years.

  2. Sodium, potassium, and calcium are prepared by the electrolysis of their respective fused chlorides.

  3. Aluminium is prepared by the electrolysis of bauxite, Al_2O_3, dissolved in molten cryolite, Na_3AlF_6.

XV.1.2. Alloys

Difinition

- An *alloy* is a metallic substance formed by melting two or more metals together. It may be a type of solid solution, an intimate mixture or a definite compound of the constituent elements.

Properties of Alloys

- The properties vary greatly with their compositton.
- Usually have a lower metling point than their constiuten metals.
- They usually resist corrosion, can be machined, cast, rolled, forged or welded easily.

Some Important Alloys

- Aluminium bronze, 90% Cu, 10% Al, for castings.
- Babbitt, 90% Sn, 7% Sb, 3% Cu, for bearings.
- Brass, 67% Cu, 33% Sn, for castings and fixtures.
- Coinage bronze, 95% Cu, 4% Sn, 1% Zn, for coins.
- German silver, 55% Cu, 25% Zn, 20% Ni, for silver imitation.
- Gold (18 carat), 75% Au, 10-20% Ag, 5-15% Cu, for jewelry.

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- Gold coinage, 90% Au, 10% Cu, for coins.
- Nichrome, 75% Ni, 12% Fe, 11% Cr, 2% Mn, for resistance wire.
- Nickel coinage (USA), 75% Cu, 25% Ni, for coins.
- Pewter, 85% Sn, 6.8% Cu, 6% Bi, 1.7% Sb, for dishes.
- Silver coinage (USA), 90% Ag, 10% Cu, for coins.
- Solder, 50% Pb, 50% Sn, for joining metals.
- Sterling silver, 92% Ag, 8% Cu, for silverware.
- Type metal, 82% Pb, 15% Sb, 3% Sn, for type.
- Wood's metal, 50% Bi, 25%Pb, 12.5% Sn, 12.5% Cd, for low melting alloys.

XV.2. The alkali metals

Introduction

- The alkali metals, lithium, sodium, potassium, rubidium, cesium, and francium, constitute the first group of the periodic system. Only sodium and potassium are of commercial importance and will be considered in detail.
- They all form soluble bases or alkalies and hence are called the alkali metals.
- They all contain one electron in the outermost energy level of their atoms, which electron is easily removed.

Physical and Chemical Properties

- These elements invariably display a valence of positive 1.
- These elements are soft and easily fusible.
- Their spectra are easily excited and their chlorides impart characteristic colors to a Bunsen flame; lithium,red; sodium, yeloww; potassium, violet; rubidium, red; and cesium, blue.
- They all decompose water vigorously liberating hydrogen and forming hydroxides.
- They all combine directly with hydrogen, carbon, nitrogen, sulfur, and oxygen.
- They are powerful reducing agents.

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XV. 2.1. Sodium

Occurrence

- The ocean contains about 2.8 per cent of sodium chloride.
- Innumerable salt lakes, salt wells, and beds of solid salt are known and worked in all parts of the world.

Preparation

- Sir Humphry Davy in 1807 first prepared metallic sodium by electrolysis of sodium hydroxide.
- Sodium is prepared ommercially today by the electrolysis of molten sodium hydroxide in the Castner and other similar cells.

$$2\ NaOH \rightarrow 2\ Na + H_2 + O_2$$

- Sodium is also prepared by the electrolysis of fused NaCl containing small amounts of $CaCl_2$ and $BaCl_2$ to lower the melting point.

Properties and Uses of Metallic Sodium

- Sodium is a soft, bright silvery metal.
- Its symbol, Na, is derived from its Latin name, "natrium".
- Atomic weight, 22.990. Atomic number, 11.
- Melting point, 97.5°C. Boiling point, 880°C.
- Specific gravity, 0.971, being lighter than water.
- It combines readily with oxygen so is preserved under kerosene or naphtha.
- It decomposes water vigorously liberating hydrogen and forming sodium hydroxide.

$$2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2 \uparrow$$

- It reacts with alcohol liberating hydrogen, *e.g.*,

$$2\ Na + O_2 \rightarrow Na_2O_2$$

- It combines directly with the halogens, sulfur, hydrogen, and other non-metals, *e.g.*,

$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

$$2\ Na + S \rightarrow Na_2S$$

$$2\ Na + H_2 \rightarrow 2\ NaH$$

- It formely was used as a reducing agent in the preparation of aluminium and magnesium.
- It is used in the preparation of the peroxide, cyanide, and amalgams.

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Compounds of Sodium

⇒ ***Sodium chloride*** (Salt), NaCl.

1. Sodium chloride is the most important compound of sodium

2. It is obtained from natural deposits by mining, by evaporation of brines, from salt wells, or freezing of brines.

3. It is used in the preparation of other sodium compounds, such as sodium carbonate, sodium bicarbonate, and sodium hydroxide.

4. It dissolves in water (35.7 g in 100 g H_2O at 0°C and 39.8 g at 100°C), a change in temeperature having little effect on its solubility.

5. The fused salt and water solution both conduct and are decomposed by an electrical current.

6. It is used in the preparation of chlorine and hydrogen chloride.

7. It is used in the manufacture of soap, as a food preservative, in freezing mixtures, and for seasoning food.

⇒ ***Sodium Hydroxide*** (Caustic Soda) (Lye), NaOH.

1. Sodium hydroxide is a deliquescent white solid, very soluble in water, and corrosive to the skin.

2. It is prepared by two distinct methods.

a) By the electrolysis of a solution of sodium chloride.

$$2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + H_2 \uparrow + Cl_2 \uparrow$$

b) By the action of slaked lime on sodium carbonate.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2\ NaOH$$

3. It is used in the refining of petroleum, the mercerizing of cotton, manufacture of viscose rayon, soap, paper pulp, hypochlorites, chlorates, and nitrites.

⇒ ***Sodium Bicarbonate*** (Baking Soda) (Saleratus), $NaHCO_3$.

1. Its most important use in baking where it is decomposed by the lactic acid of sour milk, and in the preparation of baking powders, and in fire extinguishers.

2. Huge deposits of natural carbonates are found in Owens Lake, California and Lake Magadi in British East Africa.

3. However, most of the sodium bicarbonate and sodium carbonate today are made by the *Solvay process*.

a) A saturated solution of brine is saturated to due the carbonate by heating to red heat.

$$CO_2 + NH_3 + H_2O \rightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3 \downarrow$$

b) The bicarbonate may be converted to the carbonate by heating to red heat.

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$$2\ NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O \uparrow + CO_2 \uparrow$$

c) The by-product ammonium chloride is treated with lime to recover the ammonia gas.

$$2\ NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2\ H_2O + 2\ NH_3$$

d) Limestone serves as the source of both the carbon dioxide and lime.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$

⇒ ***Sodium Carbonate*** (Soda Ash), Na_2CO_3, and (Washing Soda), (Sal Soda), (Soda Crystals), $Na_2CO_3 \cdot 10H_2O$.

1. It is prepared principally by the Solvay process.
2. It was formerly made by the *Le Blanc process* (now nearly obsolete).

a) Sodium sulfate, coke, and limestone are heated in a rotary furnace.

$$Na_2SO_4 + 4\ C \xrightarrow{\Delta} Na_2S + 4\ CO \uparrow$$

$$Na_2S + CaCO_3 \xrightarrow{\Delta} CaS + Na_2CO_3$$

b) The sodium carbonate is extracted with water or is decomposed with lime to form sodium hydroxide.

$$Na_2CO_3 + CaO + H_2O \xrightarrow{\Delta} CaCO_3 \downarrow + 2\ NaOH$$

3. It is used in washing powders, preparation of sodium salts, as weak alkali, in the preparation of sodium hydroxide, for softening water, making glass, oil refining, manufacture of soap, and the manufacture of paper.

⇒ ***Sodium Nitrate*** (Chile Salpeter), $NaNO_3$.

1. Large deposits are found in Chile and Peru.
2. Sodium nitrate is used in making nitric acid, and the manufacture of explosives and fertilizers.

⇒ ***Sodium Sulfate*** (Glauber's Salt), $Na_2SO_4 \cdot 10H_2O$.

1. Sodium sulfate is ysed in the manufacture of glass and in medicine.

⇒ ***Sodium Tetraborate*** (Borax), $Na_2B_4O_7 \cdot 10H_2O$.

1. Borax is used for softening water, the manufacture of soap, glass and welding fluxes.

⇒ ***Sodium Thiosulfate*** (Hypo), $Na_2S_2O_3 \cdot 5H_2O$.

1. Hypo is used as a "fixer" in photography.

⇒ ***Sodium Cyanide***, NaCN.

1. Sodium cyanide is used in extracting gold and silver from their ores.

⇒ ***Sodium Hypochlorite***, NaClO.

1. It is used as a bleach for cotton, and paper, also as a germicide.

⇒ ***Sodium Bromide***, NaBr, and ***Sodium Iodide***, NaI.

1. These compounds are used in medicine and photography.

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Analytical Test

- Sodium salts impart a characteristic yellow color to a Bunsen flame.
- Sodium salts may be precipitated as the pyroantimonate, $Na_2H_2Sb_2O_7$.

XV.2.2. Potassium

Occurrence

- The Stassfurt deposits of Germany produce *kainite* ($MgSO_4$, $KCl{\cdot}3H_2O$, *sylvin* (Kcl), and *carnallite* (KCl, $MgCl_2{\cdot}6H_2O$).
- Some potassium salts are obtained by extraction of wood ashes.
- Potassium compounds are also obtained from natural brines, cement mill and blast furnace dust, kelp from the ocean, and Searles Lake of California.

Preparation

- First prepared in 1807 by Sir Humphry Davy by the electrolysis of potassium hydroxide.
- It is prepared today by the electrolysis of molten potassium hydroxide.

Properties and Uses of Metallic Potassium

- Potassium is a soft, bright silvery metal.
- Its symbol, K, is derived from its Latin name, "Kalium".
- Atomic weight, 39.102. Atomic number, 19.
- Melting point, 62.3°C. Boiling point, 760°C.
- Specific gravity, 0.86.
- In all of its important chemical properties and uses it is identical with those of sodium.

Compounds of Potassium

⇒ ***Potassium Cholride***, KCl.

1. This compound is used as a fertilizer and in the preparation of all other potassium compounds.

⇒ ***Potassium Hydroxide*** (Caustic Potash), KOH.

1. It is prepared by the electrolysis of a potassium chloride solution.
2. It is used in making soft soap and as the electrolyte in the Edison storage battery.

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⇒ ***Potassium Carbonate*** (Pearl Ash), K_2CO_3.

1. Potassium carbonate is used in making soft soap, hard glass, and in the dye industry.

⇒ ***Potassium Nitrate*** (Salpeter), KNO_3.

1. This compound is used in black gunpowder, along with charcoal and sulfur.

⇒ ***Potassium Chlorate***, $KClO_3$.

1. This compound is used in making matches, explosives, fireworks, and for the laboratory preparation of oxygen.

⇒ ***Potassium Sulfate***, K_2SO_4.

1. This compound is used in the preparation of potassium alum and as a fertilizer.

Analytical Test

- Potassium compounds impart a characteristic violet color to a Bunsen flame, which is visible through cobalt glasses.
- Potassium is frequently precipitated as the perchlorate, $KClO_4$, chloroplatinate, K_2PtCl_6,or cobaltinitrite, $K_2NaCo(NO_2)O_6$.

XV.3. The alkaline earth metals

Introduction

- The members of the alkaline earth group of metals, beryllium, magnesium, calcium, strontium, barium, and radium constitute Group IIA of the periodic table.
- Four of these metals, Mg, Ca, Sr, and Ba, were discovered by Sir Humphry Davy using electrolytic methods.
- These alkaline earth metals all have two electrons in the outermost energy level of their atoms.

Group Characteristics

- All have a valence of positive two in all of their important compounds.
- Beryllium is somewhat related to aluminium, and magnesium to zinc.
- All are silvery bright metals, with toughness and malleability about equal to that of lead.
- They are all lighter than aluminium (except Ba and Ra) and all melt between 651°C (Mg) and 1350°C (Be).
- Calcium salts impart an orange, strontium a red, and barium a green color to the Bunsen flame.
- They are all very active chemically and oxidize or burn readily in air.

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- They react with water forming hydroxides and liberating hydrogen.
- They combine directly with the halogens and nitrogen.
- Their hydroxides increase and their sulfates decrease in solubility with increasing atomic weight of the metals.
- Only magnesium and calcium will be considered in detail.

Occurrence

- None of the alkaline earth metals exist free in nature.
- *Beryllium* in *beryl*, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$.
- *Magnesium* (2.27 per cent of earth's crust) in magnesite, $MgCO_3$; dolomite, $MgCO_3 \cdot CaCO_3$; carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$; talc or soapstone, $H_2Mg_3(SiO_3)_4$; asbestos, $CaMg_3(SiO_3)_4$; and spinel, $Mg(AlO_2)_2$.
- *Calcium* (3.42 per cent of the earth's crust) in limestone, marble, chalk, calcite, Iceland spar, or marble, $CaCO_3$; gypsum, $CaSO_4 \cdot 2H_2O$; fluorspar, CaF_2; apatite, $Ca_5(PO_4)_3Cl$; and phosphate rock, $Ca_3(PO_4)_2$.
- *Strontium* (0.02 per cent of earth's crust) in strontianite, $SrCO_3$; and celestite, $SrSO_4$.
- *Barium* (0.08 per cent of earth's crust) in barites, $BaSO_4$; and whiterite, $BaCO_3$.
- *Radium* in uranium minerals known as carnotite, $K_2O(UO_3)_2 \cdot V_2O_3 \cdot 3H_2O$.

XV.3.1. Magnesium

Preparation

- Metallic magnesium is prepared by the electrolysis of fused anhydrous magnesium chloride in an atmosphere of coal gas.

Properties and Uses

- Magnesium is a light, white, tough metal, tarnishing readily in air.
- Atomic weight, 24.31. Atomic number, 12.
- Melting point, 651°C. Boiling point, 1 110°C.
- Specific gravity, 1.74 at 20°C.
- Valence, positive 2.
- It burns in air with a dazzling white light, forming MgO and Mg_3N_2·

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$$2\ Mg + O_2 \rightarrow 2\ MgO$$

$$3\ Mg + N_2 \rightarrow Mg_3N_2$$

- Magnesium is even oxidized in an atmosphere of steam or carbon dioxide.

$$2\ Mg + CO_2 \rightarrow 2\ MgO + C$$

- Magnesium is a typical active metal reacting with acids.

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2\ \uparrow$$

- Magnesium is used for flash-light photography, signal flares, pyrotechnics, and alloys such as magnalium and Dow metal.

Compounds of Magnesium

⇒ ***Magnesium Oxide*** (Magnesia), MgO.

1. It is prpared by gently heating magnesium carbonate.

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

2. Fused magnesia is used for magnesia brick for furnace linings.

3. Moistened with a saturated solution of $MgCl_2$ it soon sets to a firm hard cement. (Stucco and terra cotta.)

4. It reacts with water to form the hydroxide.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

5. The flocculent form of magnesium oxide is used as a rubber filler.

⇒ ***Magnesium Hydroxide***, $Mg(OH)_2$.

1. It is used in mouth washes and infant foods where a slightly active, insoluble base is required.

⇒ ***Basic Magnesium Carbonate***.

1. Magnesia Alba, $Mg_4(OH)_2(CO_3)_3 \cdot 3H_2O$, is emplyed as a cosmetic.

2. "85 per cent-magnesia," $MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, is a light effective covering for steam pipes and boilers.

⇒ ***Magnesium Sulfate***, (Epsom salt), $MgSO_4 \cdot 5H_2O$.

1. It is used as apurgative in medicine.

2. It is also used in the dye industry, for tanning leather, and the manufacture of paint and soap.

⇒ ***Basic Silicates*** (Asbestos, Talc, Serpentine, Meerschaum).

1. Asbestos is used for fireproof theater curtains, automobile brake linings, steam pipe coverings, cement and shingles.

2. Talc is used in toilet articles and for sizing paper.

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=> ***Magnesium Citrate***, $Mg_3(C_6H_5O_7)_2$.

1. This compound is used in medicine.

Analytical Test

- Magnesium is usually precipitated as a magnesium ammonium phosphate.

$$MgCl_2 + Na_2HPO_4 + NH_4OH \rightarrow 2\ NaCl + H_2O + MgNH_4PO_4 \downarrow$$

1. Other alkaline earth and heavy metals must be absent.
2. When ignited it forms magnesium pyrophosphate, $Mg_2P_2O_7$.

XV.3.2. Calcium

Preparation

- Metallic calcium is prepared by the electrolysis of the molten chloride.

Properties and Uses

- Calcium is a silvery white metal, that readily corrodes in air.
- Atomic weight, 40.08. Atomic number, 20.
- Melting point, 810°C. Boiling point, 1 439°C.
- Specific gravity, 1.54 at 29°C.
- Valence, positive 2.
- Calcium reacts slowly with water even at room

$$Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2 \uparrow$$

- Calcium combines directly with all the non-metals and hydrogens, *e.g.*,

$$Ca + H_2 \rightarrow CaH_2$$

- It burns with a brilliant crimson flame in air forming CaO.
- The only important alloy is Frary metal (Ca and Ba), used for bearings.
- It is used to a limited extent as a reducing agent and for drying organic compounds.

Compounds of Calcium

⇒ ***Calcium Carbonate***, (Limestone, Marble, Chalk, Calcite, Iceland spar, Marl), $CaCO_3$.

1. The finer, harder grades are used extensively for building stone.
2. It is used in the manufacture of Portland cement.
3. It is used in the preparation of quicklime, CaO.

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$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \uparrow$$

4. It is used as a flux in the smelting of iron, copper, zinc and other metals.

5. It is used in the manufacture of glass.

6. It is used for liming acid soils.

7. Calcium carbonate reacts with inorganic acids.

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

(a) The CO_2 turns lime water milky and these facts may be used as a test for the original carbonate.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$

8. Calcium carbonate is soluble in a solution of carbonic acid.

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2 \quad \text{(soluble)}$$

(a) This reaction accounts for the formation of limestone caves, stalactites and stalagmites.

⇒ ***Calcium Oxide***, (Quicklime), CaO.

1. Calcium oxide is prepared by the calcination of limestone in vertical furnaces or rotary kilns.

2. It is used for the production of mortar, plaster, slaked lime, and bleaching power.

3. It reacts with water forming the hydroxide (slaked lime).

$$CaO + H_2O \rightarrow Ca(OH)_2$$

⇒ ***Calcium Hydroxide***, (Slaked lime), $Ca(OH)_2$.

1. It is a slightly soluble base.

2. It is used to soften water, in dehairing hides in tanning, for acid soils, making glass, and mortar.

(a) Mortar contains calcium hydroxide, water, sand, and binding material as hair.

(b) During setting the carbon dioxide of the air reacts to form calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

(c) Mortar of this type will not set under water.

⇒ ***Calcium Sulfate***, (Gypsum), $CaSO_4 \cdot 2H_2O$, and (Plaster of Paris), $(CaSO_4)_2 \cdot H_2O$.

1. Gypsum is used as a fertilizer.

2. Plaster of Paris is made by heating gypsum to about 125°C.

(a) $2\,CaSO_4 \cdot 2H_2O \underset{\text{Setting}}{\overset{\text{Preparation}}{\longleftrightarrow}} (CaSO_4)_2 \cdot H_2O + 3\,H_2O$

(Gypsum) (Plaster of Paris)

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(b) Water is added to set the Plaster of Paris for casts, stucco, plaster, and plaster board.

⇒ ***Calcium Hypoclorite***, (Bleaching Powder), $CaOCl_2$.

1. It is prepared by passing chlorine over slaked lime.

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$

⇒ ***Calcium Carbide***, (Carbide), CaC_2.

1. It is prepared by heating lime and coke in an electric furnace.

$$CaO + 3\,C \xrightarrow{\Delta} CaC_2 + CO$$

2. It is used in preparing acetylene and calcium cyanamide.

$$CaC_2 + 2\,H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

⇒ ***Calcium Phosphate***, (Rock Phosphate), $Ca_3(PO_4)_2$.

1. It is used in the preparation of phosphorus and fertilizers.

⇒ ***Calcium Chloride***, $CaCl_2$.

1. The anhydrous salt is frequently used to absorb moisture in drying gases.
2. It is used for allaying dust on roads, race tracks, and tennis courts.
3. It is used in refrigerating brines.

⇒ ***Calcium Nitrate***, $Ca(NO_3)_2 \cdot 4H_2O$.

1. It is often produced in the fixation of nitrogen by the arc process, and is used as a fertilizer.

Analytical Test

- Calcium salts color a Bunsen flame a brick red.
- Calcium is frequently precipitated as the carbonate, $CaCO_3$, or oxalate, CaC_2O_4.

XV.3.3. Water Softening

Definition of Hard Water

- *Härd water* contains soluble calcium, magnesium, and iron salts.

1. Hard water forms deposits (scale) on the inside of steam and hot water pipes and boilers.
2. Hard water precipitates soap from solution forming insoluble curds.

$$2\,C_{17}H_{35}COONa\ (\text{Sodium soap}) + Ca^{++}\ (\text{or } Mg^{++}) \rightarrow (C_{17}H_{35}COO)_2Ca \downarrow + 2\,Na^{+}$$

Types of Hard Water

- Temporary Hard Water.

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1. Temporary hardness is due to the presence of acid carbonates.
2. Temporary hard water loses its hardness when boiled, *e.g.*,

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

3. The bicarbonates may also be removed by lime treatment,*e.g.*,

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 \downarrow + 2\ H_2O$$

- Permanent Hard Water.
  1. Permanent hardness is due to the presence of other salts of calcium and magnesium.
  2. Permanent hardness is most often removed by soda ash (Na_2CO_3) treatment, *e.g.*,

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$

$$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 \downarrow + 2\ NaCl$$

  3. Magnesium salts may precipitate as hydroxides, *e.g.*,

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$$

- Both types of hardness may be removed by filtration through certain artificial zeolites (Permutite), *e.g.*,

$$Na_2(Al_2Si_2O_8) + Ca^{++}\ (\text{or } Mg^{++}) \rightarrow Ca(Al_2Si_2O_8) + 2\ Na^+$$

  1. The spent zeolite is regenerated by treatment with strong brine (NaCl) restoring the original zeolite, $Na_2(Al_2Si_2O_8)$.

XV.4. Aluminium and ceramics

Historical

- Discovered in 1825 by Oersted.
- First practical electrical method of extraction patented by Cowles in England and the United States in 1885.
- Present electrolytic method of reduction of the oxide in molten cryolite discovered simultaneously by Hall in America and Héroult in France in 1886.
- In 1856 the price of aluminium was $90.00 a pound, in 1886 about $5.00 a pound, and in 1953 it was 22 c.

Occurrence

- Aluminium ranks third in abundance, forming 7.84 per cent of earth's crust.
- In aluminosilicates.
  1. Feldspars as $KAlSi(Si_2O_4)_2$.
  2. Micas as $H_2KAl_3(Si_2O_4)_3$.

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3. Clays (kaolin) as $H_4Al_2Si_2O_9$.

- Cryolite, Na_3AlFe_6, and Bauxite, $Al_2O_3 \cdot 2H_2O$, are important sources of the metal.
- Ruby, sapphire, and corundum are forms of the oxide.
- Garnets, $(Ca \cdot Mg \cdot Fe)(Al \cdot Fe)_2(SiO_4)_3$; and torquoise, $Al_2(OH)_3PO_4 \cdot H_2O$, colored with copper phosphate.

Preparation

- First prepared commercially (1850) by the reduction of the chloride with sodium at high temperatures.
- Today by electrolysis of bauxite, Al_2O_3, in molten cryolite, Na_3AlFe_6, (Hall Process).
  1. Large iron pots with a thick carbon lining act as the cathode.
  2. A number of large graphite rods serve as the anode.
  3. The cryolite is melted by the heat of the arc.
  4. Bauxite is then added, deomposed, and the molten aluminium collects at the cathode. Oxygen is liberated at the anode.
  5. The temperature of the bath is held at about 1 000°C.
  6. The aluminium produced is about 99.0 to 99.5 per cent pure.

Physical Properties

- The metal is white and extremely light, density, 2.7.
- Atomic weight, 26.98. Atomic number, 13.
- Melting point, 658.7°C. Boiling point, 1 800°C.
- Its conductivity is 60 per cent that of copper, but weight it is twice as good a conductor.
- Aluminium stands second in malleability, and sixth in ductility among the metals.
- The metal has a silvery appearance, but soon acquires a dull white luster, due to a firm coat of oxide that protects the surface from further oxidation.

Chemical Properties

- Valence, positive 3.
- Aluminium does not rust readily, but if heated to redness burns with a brilliant white light.

$$4\,Al + 3\,O_2 \xrightarrow{\Delta} 2\,Al_2O_3$$

- Aliminium combines with nitrogen when heated.

$$2\,Al + N_2 \xrightarrow{\Delta} 2\,AlN$$

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- Aluminium dissolves readily in hydrochloric acid, slowly in sulfuric acid, but is rendered passive by nitric acid.

$$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2 \uparrow$$

$$2\ Al + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2 \uparrow$$

- Dilute alkalies attack aluminium.

$$2\ Al + 2\ NaOH + 2\ H_2O \rightarrow 2\ NaAlO_2 + 3\ H_2 \uparrow$$

Uses

- Household utensils, furniture, and construction.
- Light weight construction for airplaines, automobiles, and railroad coaches.
- Foil, as a substitute for tin foil, and as a "silver" paint.
- Electrical transmission lines.
- As a "scavenger" to remove dissolved oxygen in the iron and steel industry.
- In "thermite" welding of iron.
- Production of important alloys as magnalium, duralumin, and alclad.
- Flashlight bulbs for indoor photography.

Analytical Test

- Qualitatively and quantitatively, aluminium is usually separated from other positive ions and identified as the hydroxide, and weighed as the oxide.
- Aluminium hydroxide when fused with cobalt nitrate solution produces a blue residue.

Compounds of Aluminium

⇒ ***Aluminium oxide***, Al_2O_3.

1. Corundum and emery for abrasives.
2. Ruby and sapphire for gems.
3. Alundum is a synthetic abrasive and is also used in making refractory crucibles.
4. Artificial rubies and sapphires are now produced in large quantities.
5. The ore from which aluminium is extracted.

⇒ ***Aluminium hydroxide***, $Al(OH)_3$.

1. Used as mordant in the dye industry.
2. Used for the clarification of water.
3. It is amphoteric in nature, *e.g.*,

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$$Al(OH)_3 + 3\ HCl \rightarrow AlCl_3 + 3\ H_2O$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2\ H_2O$$

⇒ ***Aluminium chloride***, $AlCl_3$.

1. It is used extensively in the petroleum industry as a catalyst in the production of gasoline by cracking.

2. As a catalyst in organic reactions.

3. Prepared now by the action of chlorine on bauxite in the presence of carbon. (McAfee process)

4. Price recently reduced from $1.50 to 15c a pound as a result of the McAfee process.

⇒ ***Aluminium sulfate***, $Al_2(SO_4)_3 \cdot 18H_2O$.

1. Used in the purification of water, mordant in dyeing, sizing of paper, and tanning of leather.

⇒ ***Alums***.

1. Alums are double sulfates of a tri- and mono-valent cation, $M^+M^{+++}(SO_4)_2 \cdot 12H_2O$.

(a) The mono-valent cation may be Na^+, K^+, NH_4^+, Rb^+, Cs^+, Tl^+, or Ag^+.

(b) The tri-valent cation may be Al^{+++}, Fe^{+++}, Cr^{+++}, Mn^{+++}, Ti^{+++}, Tl^{+++}, Co^{+++}, Ga^{+++}, V^{+++}, or Rh^{+++}.

2. The sodium alum, $NaAl(SO_4)_2 \cdot 12H_2O$; potassium alum, $KAl(SO_4)_2 \cdot 12H_2O$; and ammonium alum $NH_4Al(SO_4)_2 \cdot 12H_2O$, are most important.

(a) Used in alum baking powders, fire extinguishers, mordants in dyeing, clarification of water, sizing of paper, and fireproofing fabrics.

⇒ ***Thermite***.

1. A mixture of powdered metallic aluminium and ferric oxide, used for welding iron, breaking ice jams, and wrecking steel structures.

2. Temperatures as high as 3 000°C may be obtained.

3. Other alloying metals may be added to the mixture.

4. Produces a strong, economical weld.

5. Other metallic oxides may be reduced with metallic aluminium (Goldschmidt process), *e.g.*, Mn, Cr, Ti, Mo, U, W, B, and Si.

6. Equation: $Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe + 185\ 000$ cal.

Ceramics

Clay or Koalin, $H_4Al_2Si_2O_9$.

- Formed by disintegration of granite and related recks.
- Basis for bricks, pottery, tile, porcelain, Chinaware, stoneware, etc.

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- Common grades are Ball clay, China clay, fireclay, Fuller's earth, shale, and slate.

Classification of Ceramic Products

⇒ ***Unglazed porous material, as bricks, pottery, and terra-cotta.***

1. Clay is kneaded with water, shaped and heated until it begins to vitrify.

2.May be shaped by pressing into molds, on a potter's wheel, or pouring a thin clay suspension into plaster of Paris forms.

⇒ ***Porous material, glazed superficially, as earthenware, and sanitary ware.***

1. A glaze may be applied to the surface before firing, or produced by throwing salt, NaCl, into the fire.

⇒ ***Non-porous material, as stoneware, Chineware, and porcelain.***

1. Bone china is molded from bone ash, kaolin, and feldspar.
2. Usually fired to a higher temperature.
3. A glaze of felspar is frquently applied.
4. Porcelain is made of white clays (kaolin), quartz, and powdered feldspar.

(a) Fired at a low temperature, glaze applied, and then throughly vitrified.

Portland Cement

- Definition.

1. Portland cement consists of a mixture of complex silicates and aluminates of calcium, and possess the property of hardening in either air or under water.

- Manufacture.

1. By combining limestone, marl, or chalk with clay, shale, slate rock or blast-furnace slag.

2. The materials are ground, 4 to 5 parts of limestone to 1 of clay or shale. They may be ground dry, or with water (wet process) to form "slurry".

3. The dry mix, or "slurry" is heated to 1 400° to 1 600°C, in a rotary kiln producing clinker.

4. The clinker is cooled and intimately ground with 2 to 3 per cent of gypsum, which retards the setting time.

- Composition of Portland Cement.

1. The composition varies and has no definite formula.

2. Content of Na_2O or K_2O must be low. MgO must not exceed 5 per cent and SO_3, 3 per cent.

3. Ratio of (CaO + MgO) to (SiO_2 + Al_2O_3) should be between 2.5 and 4.0.

4. Ratio of SiO_2 to Al_2O_3 should be between 2.5 and 4.0.

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5. Such a cement contains approximately: CaO, 64 per cent; SiO_2, 22 per cent; Al_2O_3, 7 per cent; FeO, 4 per cent; SO_3, 1.6 per cent; MgO, 0.8 per cent; Na_2O and K_2O, 0.6 per cent.

- Setting of Portland Cement.
  1. Initial set due to the formation of crystals of calcium silicate and calcium aluminate.
  2. During final hardening, crystals of calcium hydroxide may appear.
  3. The setting is partially a colloidal phenomenon.

XV.5. Iron and steel

XV.5.1. Iron

Introduction

- Iron articles were made by the Egyptians and Assyrians as early as 3 000 B.C.
- The Romans exploited the iron mines of Spain for their supply of iron.
- Iron is the fourth most abundant element comprising 4.44 per cent of the earth's crust.
- Iron derives its symbol, Fe, from the Latin name, "ferrum."

Occurrence

- The most important ore is hematite (red ocher or rouge), Fe_2O_3.
- Other ores of lesser importance are limonite, $Fe_2O_3 \cdot 3H_2O$, magnetite, Fe_3O_4, siderite, $FeCO_3$, and taconite (51% SiO_2 and 27% Fe).
- Iron occurs free in meteorites.
- Iron pyrite (Fool's Gold), FeS_2, is used in the manufacture of sulfuric acid but has no importance as a source of iron.
- Important producers are Minnesota, Michigan, Alabama, Germany, France, Belgium, England, Sweden, Russia, Labrador and Venezuela.

Metallurgy

- Hematite, Fe_2O_3, is reduced with carbon (coke).
- Materials used.
  1. *Iron ore*, usually hematite (Fe_2O_3).
  2. *Carbon*, usually in the form of coke, is used.

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3. A *flux* is added, usually limestone to react with the silicious gangue to form a light fusible slag. Sand may be added as a flux to ore that are roch in carbonates.

4. *Hot air* is introduced to aid the combustion and reduction.

- The Blast Furnace.

1. The blast furnace may be 75 feet high and 20 feet inside diameter at the widest point.
2. The walls are several feet thick and are lined with fire-brick.
3. The ore, coke, and flux areadded through an air-tight locker valve at the top.
4. Hot air is blown into the furnace near the bottom through *tuyeres* for the blast.
5. The reduced metal colects in the bottom of the furnace, and the slag on the surface of the molten metal.
6. The molten metal is tapped off every 6 hours and cast into molds or taken to the Bessemer converter to be made immediately into steel.
7. The slag is withdrawn at a second tap-hole above the other.

(a) The slag may be discarded, used to make paving stone, mineral wool or cement.

8. The blast furnace also produces vast quantities of carbon monoxide (blast-furnace gas).

(a) A single furnace may produce over 100,000,000 cubic feet of gas a day.

(b) A large portion of this gas is burned to heat the air blast, drive the machinery about the steel plant, or to produce steel.

9. The blast furnace produces pig iron.
10. A large blast furnace may require 1 000 tons of iron ore, 500 tons of coke, and 250 tons of limestone, and produce 550 tons of pig iron every 24 hours.
11. Blast furnace reactions:

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$

400(– 800(X

$$CaCO_3 \rightarrow CaO + CO_2$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$

800(– 1 000(X

$$C + O_2 \rightarrow CO_2$$
$$C + CO_2 \rightarrow 2\ CO$$

1 000(– 1 500(X

- Several large steel producers have joined in the development of Minnesota magnetic taconite deposits as future sources of commercial iron.

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1. Taconite may be magnetic or nonmagnetic.

2. The magnetic type is ground wet as fine as flour.

3. The iron mineral is concentrated by magnetic separation and filtration.

4. The concentrate is formed into balls, or pellets, of approximately 1 in, by burning at 2300°F, and contain about 60% iron.

5. Long-range development plans call for an annual production of 15,000,000 tons.

6. The use of the nonmagnetic taconite is far more difficult, and at present an unsolved problem.

Pig Iron and Cast Iron

- Pig iron contains 3.5 to 4.0 per cent of carbon, 0.75 to 2.00 per cent of silicon, 0.50 to 1.50 per cent of manganese, and traces of sulfur and phosphorus.
- The impurities lower the melting point of the iron from 1 535° to about 1 130°C.
- Pig iron has low tensile strength.
- Mixed with scrap iron (cast iron) it is used for casting stoves, steam radiators, window weights, etc.
- Malleable iron, with a low phosphorus content, is used for agricultural implements, tools and machines.

Wrought Iron

- The *puddling process*, invented by Cort in England in 1874, is used to prepare wrought iron.

1. Iron nearly free from sulfur and phosphorus is used.

2. Iron oxide or rusty iron is added.

3. The charge is heated in a reverberatory furnace.

4. The carbon, manganese, and silicon are oxidized at the expense of the oxygen in the ferric oxide.

5. The pasty pure iron with slag is then put through rolls which squeeze out most of the slag.

6. Wrought iron is used for pipe, bolts, chains, fencing, horseshoes and grate bars.

7. It can not be tempered or annealed since it contains very little carbon.

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XV.5.2 Steel

Definition

- Iron which contains 0.5 to 2.0 per cent of carbon and usually manganese and which can be hardened when quenched is called *steel.* Most steels have high tensile strength, toughness and hardness.

Manufacture of Steel

- Bessemer Steel.
  1. Bessemer steel is produced by burning the impurities from molten pig iron with a blast of air in an egg-shaped furnace.
  2. Carbon and manganese (spiegeleisen) is then added.
  3. Bessemer steel is used for rails, wire, rods, bars, concrete reinforcement, axles, etc.
- Open-hearth Steel.
  1. Open-hearth steel is made by removing the impurities from molten pig iron by oxidation with ferric oxide.
  2. The process and furnace are somewhat similar to those described for wrought iron.
  3. About 80 per cent of all steel produced today is Open-hearth steel and is used for rail, bridge girders, armor plate, wire, nails, etc.
- Crucible Steel.
  1. Crucible steel is made by melting wrought iron in a closed fire-clay-graphite crucible in contact with charcoal.
  2. Crucible steel contains 0.75 to 1.5 per cent of carbon.
  3. Crucible steel is used for watch springs, razors, knives, and tools.
- Electrical Steel.
  1. Electrical steel is produced by controlling its composition while being held in a molten condition in an electric furnace.
  2. Electrical steel is used in automobile engines, transmission systems, axles, and wheels.

Classification of Steels

- Carbon Steels.
  1. Carbon steels owe their properties to the presence of carbon and manganese (up to about 1.5 per cent of each) and the heat treatment applied.
- Alloy Steels.
  1. Alloys steels are made by the addition of other metals or an increased quantity of manganese to simple steels.

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2. *Manganese steel* contains 11 to 14 per cent manganese, is usually hard, and resistant to wear. It is used for safes, armor plate, and teeth for steam shovels.

3. *Chromium steels* (Stainless steels) contain 1.5 to 15 per cent of chromium and have a hard, tough, strong surface and are resistant to corrosion.

4. *Nickel steel* contains 2 to 4 per cent of nickel, and has high tensile strength, low coefficient of expansion, and high resistance to corrosion.

5. *Silicon steels* contain 1 to 16 per cent silicon.

(a) Low content silicon steels are hard and not easily broken. They are used in electrical transformers.

(b) High content silicon steels are acid resistant. (Duriron.)

6. *Tungsten steel*, containing 4 to 6 per cent of tungsten, retains its temper when heated and is used for lathe tools.

7. *Vanadium steel*, containing 1 to 2.5 per cent of vanadium, is shock proof and is used in automobile parts.

8. *Molybdenum steel* contains 4 to 5 per cent of molybdenum and has high tensile sterngth and resistance to acid corrosion. it is used in making high-speed tools.

Heat Treatment of Steels

- Annealing.

1. Annealing is heating steel to a bright red heat and then slowly cooling.

2. Such steel is soft and pliable and wears better than wrought iron.

- Hardening.

1. Hardened steel is produced by heating steel to bright redness and then suddenly cooling in oil or water.

2. Such steel is hard and brittle.

- Tempering.

1. Any degree of hardness may be obtained by heating hardened steel to a temperature much below redness and slowly cooling.

2. Wrought iron can be tempered because it contains very little carbon.

- Sulfur.

1. Excessive quantities of sulfur make iron and steel brittle while hot (hot short).

- Phosphorus.

1. Excessive quantities of phosphorus make iron and steel brittle while cold (cold short).

- Case Hardening.

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1. Strong, flexible, mild (low-carbon) steel is given a thin coating of hardened (high-carbon) steel by heating the steel in contact with charcoal and quenching in oil.

2. Case-hardened steel is used for axles for raylroad cars, etc.

- Nitriding.

1. Special steels are heated in an atmosphere of ammonia at 630° to 655° for 2 to 90 hours.

2. The surface becomes impregnated with hard iron nitride.

XV.5.3. Pure Iron and Iron Compounds

Preparation

- Pure iron may be prepared by electrodeposition from ferrous sulfate solution.
- It may also be prepared by reduction of pure oxide with hydrogen and aluminium.

Physical and Chemical Properties

- Pure iron is silver-white, very ductile and malleable.
- Atomic wieght, 55.85. Atomic number, 26.
- Melting point, 1 535°C. Boilling point, 3 000°C.
- Specific gravity, 7.85 to 7.88.
- Valence, positive 2 (ferrous), 3 (ferric), and 6 (ferrates).
- Iron exists in several allotropic forms.

1. α-ferrite is soft, ductile, and magnetic. It is stable below 766°C.

2. β-iron is stable between 766° and 895°C.

3. γ-iron is but slightly magnetic and forms solid solutions with iron carbide. It is stable between 895° and 1 400°C.

4. δ-iron is stable between 1 400° and the boiling point of iron.

Compounds of Iron

⇒ ***Ferrous compounds*** are usually light green in color while ferric salts are usually yellow to brown.

⇒ ***Ferrous sulfate*** (green vitriol), $FeSO_4 \cdot 7H_2O$.

1. It is used as a mordant, disinfectant, in the preparation of ink, and as a weed killer.

⇒ ***Ferric alum***, $KFe(SO_4)_2 \cdot 12H_2O$.

1. It is used principally as a mordant.

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⇒ ***Potassium ferrocyanide***, $K_4Fe(CN)_6$.

1. It is used in preparing potassium cyanide, casehardening of steel, and as an analytical reagent in testing for ferric salts.

⇒ ***Potassium ferricyanide***, $K_3Fe(CN)_6$.

1. It is used in the preparation of *blue print paper*.
   (a) Strong paper is treated with solutions of ferric ammonium citrate and potassium ferricyanide.
   (b) Exposure to light reduces the ferric salt to a ferrous condition.
   (c) The print is fixed by washing in water which causes the ferrous iron to react with the potassium ferricyanide producing an insoluble dark blue precipitate of Turnbull's blue.
2. It is also used as an analytical reagent in testing for ferrous iron.

⇒ ***Ferric oxide*** (Venetian red or rouge), Fe_2O_3.

1. It is used extensively as a paint pigment for painting barns and steel, and as an abrasive in polishing plate glass.

⇒ ***Ferrous sulfide***, FeS.

1. It is prepared by heating iron and sulfur together.

$$Fe + S \xrightarrow{\Delta} FeS$$

2. It is used in the laboratory for generating hydrogen sulfide.

$$FeS + 2\,HCl \rightarrow FeCl_2 + H_2O\uparrow$$

Analytical Test

- Ferrous compounds give a blue color with potassium ferricyanide.

$$3\,FeCl_2 + 2\,K_3Fe(CN)_6 \rightarrow 6\,KCl + Fe_3[Fe(CN)_6]_2$$

(Turnbull's blue)

- Ferric compounds give a blue color with potassium ferrocyanide.

$$4\,FeCl_3 + 3\,K_4Fe(CN)_6 \rightarrow 12\,KCl + Fe_4[Fe(CN)_6]_3$$

(Prussian blue)

- Ferric salts (in the absence of mercuric compounds, nitric acid, acetates, or halide salts) give an intense red color with potassium sulfocyanate.

$$FeCl_3 + 3\,KCNS \rightarrow 3\,KCl + Fe(CNS)_3$$

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XV.6. COBALT AND NICKEL

XV.6. 1. Common Characteristics of Iron, Cobalt, and Nickel

- These elements constitute the three members of the first transition series of elements where the electrons in the third quantum state are being increased from 8 to 18.
- Differences in structure exist in the lower rather than outer electron shells.
- They have similar appearance, melting points, densities, and valence.
- All are magnetic.
- Iron, cobalt, and nickel all form complex salts.
    1. $K_4Fe(CN)_6$, $K_4Co(CN)_6$, and $K_2Ni(CN)_4$.

XV.10.2. Cobalt

- Historical.
    1. Discovered by Brandt in 1735.
    2. Named from Greek (kobold) meaning goblin or evil spirit.
- Occurrence.
    1. As an arsenide or sulfide.
    2. Associated with iron, nickel, copper, and silver.
    3. Comes from the silver-cobalt-nickel veins of Ontario, Canada.
- Preparation.
    1. Reduction of the oxide with carbon or aluminium.
- Physical Properties.
    1. A bright silvery metal with a slight reddish tinge.
    2. Atomic weight, 58.93. Atomic number, 27.
    3. Melting point, 1 480°C. Boiling point, 2 900°C.
    4. Density, 8.9 at 20°C.
    5. The metal is malleable and ductile.
- Chemical Properties.
    1. Valence, positive 2, 3, and 4.
    2. It is easily oxidized or corroded by acids.
- Uses.
    1. Special steels (stellite) for cutlery, surgical instruments, lathe tools and for permanent magnets.
    2. Cobalt salts are used to produce brilliant blue colors in porcelain, glass, tiles, and enamels.
- Cobalt Compounds.

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1. Cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$.
    (a) Used in fusion tests for zinc and aluminium.
2. Cobalt chloride, $CoCl_2 \cdot 6H_2O$.
    (a) Has the unusual property of changing color (blue to red) with changing humidity due to the changing amounts of water of crystallization in the salt.
    (b) Used for sympathetic ink and moisture indicators.
3. Cobalt oxide, CoO.
    (a) It forms important pigments when fused with certain negative oxides, *e.g.*, smalt, cobalt blue, cobalt green, and turquoise green.

- Analytical Test.
    1. Cobalt compounds impart a blue color to borax beads.
    2. Cobalt compounds produce a yellow precipitate, $K_3Co(NO_2)_6$, with potassium nitrite in acetic acid solution.

XV.6.3. Nickel

- Historical.
    1. Discovered by Cronstedt in 1751.
    2. Isolated from "kupfernickel," a German word for "copper" and "Old Nick," and hence was called nickel.
- Occurrence.
    1. Associated with copper and iron as sulfides.
    2. Comes principally from Sudbury district of Ontario, Canada.
    3. Smaller amounts come from New Caledonia, Norway, and Germany.
- Preparation.
    1. The ore is first roasted and then reduced with carbon or carbon monoxide.
- Physical Properties.
    1. Pure nickel is extremely hard, brilliant, and resistant to oxidation and acids.
    2. Atomic weight, 58.71. Atomic number, 28.
    3. Melting point, 1 452°C. Boiling point, 2 900°C.
    4. Density, 8.90.
    5. It is malleable, ductile, and tenacious.
- Chemical Properties.

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1. Valence, positive 2 and 3.
2. Extremely resistant to oxidation or corrosion by acids.
3. Powerful oxidizing agents render it passive.

- Uses.
  1. For numerous alloys, *e.g.*, nickel steel, German silver, cionage metal, Monel metal, and electrical resistance alloys, (Nichrome and Constantan).
  2. Electrodeposition of nickel is used as a protective coating for other metals.
  3. Nickel crucibles are used for chromite and caustic fusions.
  4. For a catalyst in the hydrogenation of oils.
  5. For electromagnets, (Permalloy).
- Nickel Compounds.
  1. Nickel sulfate, $NiSO_4$, and nickel ammonium sulfate, $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$.
     (a) Used in electroplating baths.
  2. Nickel oxides, NiO, and Ni_2O_3.
     (a) Used in the Edison storage cell.
     (b) As a costituent of the "under body" or first coating in enameling steel.
- Analytical Test.
  1. Nickel compounds impart a brown color to borax beads.
  2. Dimethyl glyoxime, in dilute NH_4OH, produces a beautiful strawberry red precipitate with nickel salts.
  3. Nickel may be weighed as nickel glyoxime, as the oxide, NiO, or as the metal after electrical deposition.

XV.7. Chromium and manganese

XV.7.1. Chromium

- Historical.
  1. Discovered in 1797 by Vauquelin.
  2. Name derived from the Greek word, "chroma," which means "color".
- Occurrence.
  1. The principal chromium ore is *chromite*, $Fe(CrO_2)_2$.
  2. Chromium is also responsible for the red color of rubies, and the green color of emeralds.
- Preparation.

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1. *Ferrochrome* is prepared by the reduction of chromite with carbon in an electric furnace.
   (a) It contains 60 to 70 % chromium, 1 to 8 % carbon, and the balance iron.
   (b) This is the principal form in which chromium is used industrially.
   (c) $Fe(CrO_2)_2 + 4\ C \rightarrow Fe + 2\ Cr + 4\ CO$
2. Pure chromium is prepared by the reduction of chromic oxide with aluminium. (Goldschmidt process.)
3. Chromium compounds are prepared by fusing the ore with sodium carbonate in air.
   (a) $4\ Fe(CrO_2)_2 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ Na_2CrO_4 + 8\ CO_2$
   (b) The sodium chromate is extracted with water.

- Physical Properties.
  1. Chromium is a very hard, brittle, brilliant silvery metal.
  2. Atomic weight, 51.996. Atomic number, 24.
  3. Melting point, 1 615°C. Boiling point, 2 200°C.
  4. Density, 7.1 at 20°C.
  5. It fails to tarnish even in moist air.
- Chemical Properties.
  1. Valence, positive 2, 3 and 6.
  2. Chromium resists the action of nitric acid, salt water, sulfur compounds in petroleum, and other corrosive reagents.
  3. Metallic chromium burns in air, and is attacked by the halogens, hydrochloric and sulfuric acids.
  4. The chromate and dichromate ions in acid solution are powerful oxidizing agents.

$$6\ HCl + 2\ K_2CrO_4 \rightarrow 4\ KCl + 2\ CrCl_3 + 8\ H_2O + 3\ Cl_2\ \uparrow$$

$$K_2Cr_2O_7 + 6\ KI + 7\ H_2SO_4 \rightarrow 4\ K_2SO_4 + Cr_2(SO_4)_3 + 3\ I_2 + 7\ H_2O$$

  5. The chromous ion is an effective reducing agent.

$$2\ Cr(OH)_2 + 2\ H_2O \rightarrow 2\ Cr(OH)_3 + H_2$$

  6. Chromic hydroxide, $Cr(OH)_3$, has decided amphoteric properties.

$$Cr(OH)_3 + NaOH \rightarrow NaCrO_2 + 2\ H_2O$$

$$2\ Cr(OH)_3 + 3\ H_2S \rightarrow Cr_2S_3 + 6\ H_2O$$

  7. Chromic ions form numerous coordination complexes, *e.g.*, $Cr(NH_3)_6Cl_3$, $K_3Cr(CNS)_6$, and $K_3Cr(CN)_6$.
- Uses.
  1. Ferrochrome is used for toughening and hardening steel.
  2. Preparation of alloys. For example: stainless steel, electrical resistance wire.

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3. Chromium plating is non-tarnishable, much harder than nickel, and adheres better to many metals.

(a) Used for automobile parts and domestic appliances.

4. Chromium salts are used in the tanning of leather.

- Chromium compounds.
  1. Lead chromate (Chrome yellow), $PbCrO_4$, is an important yellow paint pigment.
  2. Chromic oxide (Chrome green), Cr_2O_3, is a green pigment used in coloring porcelain and Chinaware.
  3. Sodium chromate, $Na_2CrO_4 \cdot 10H_2O$, and sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$, are important oxidizing agents.
- Valence Changes of Chromium.
  1. Cr^{++} + air $\rightarrow$ Cr^{+++}.
  2. Cr^{+++} + vigorous reducing agents $\rightarrow$ Cr^{++}.
  3. Cr^{+++} + vigorous oxidizing agents $\rightarrow$ Cr^{++++++}.
  4. Cr^{++++++} + reducing agent $\rightarrow$ Cr^{+++}.
  5. Chromate + acid $\rightarrow$ Dichromate, *e.g.*,.

$$2\ K_2Cr_2O_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

  6. Dichromate + base $\rightarrow$ Chromate, *e.g.*,.

$$Na_2Cr_2O_7 + 2\ NaOH \rightarrow 2\ Na_2CrO_4 + H_2O$$

- Analytical Test.
  1. Chromous and chromic compounds are converted to chromates by the use of sodium peroxide.
  2. Chromates may then be precipitated as yellow lead chromate, $PbCrO_4$, in dilute nitric acid solution.
  3. Chromium may be separated and weighed as Cr_2O_3.
  4. Dichromates may be titrated against the ferrous ion, or added to an excess of iodine in acid. The excess iodine is then titrated with thiosulfate.

XV.7.2. Manganese

- Historical.
  1. Discovered in 1774 by Gahn.
  2. The name is derived from the Latin, "magnes" meaning "magnet."
- Occurrence.

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1. Constitutes about 0.08 per cent of the earth's crust.
2. The most important ore is *pyrolusite*, or manganese dioxide, MnO_2, usually associated with iron ore.
3. Manganese occurs in traces in most soils and plants.
4. Present supply comes largely from Russia, Brazil, and Cuba.

- Preparation.
  1. Manganese ores, together with those of iron, are reduced in a blast furnace for the production of ferro-manganese (70 to 80% Mn) and spiegel-eisen (15 to 25% Mn).
  2. High grade ores are reduced with carbon in an electric furnace.
  3. The pure metal is produced by reduction with metallic aluminium, sodium, or magnesium. (Goldschmidt process.)
- Physical Properties.
  1. Pure manganese is a hard, brittle, gray metal that resembles iron in its general appearance.
  2. Atomic weight, 54.94. Atomic number, 25.
  3. Melting point, 1 260°C. Boiling point, 1 900°C.
  4. Density, 7.2.
- Chemical Properties.
  1. Valence, positive 2, 3, 4, 6 and 7.
  2. Manganese is easily oxidized and is decidelly more active than iron.
  3. The introduction of manganese into steel imparts toughness and improves the rolling and forging qualities of the steel.
  4. Manganese with a valence of 2 and 3 is basic; valence of 4, amphoteric; and valences of 6 and 7, acidic.
- Uses.
  1. Production of alloys, *e.g.*, spiegeleisen, manganese bronze, and manganin.
- Manganese Compounds.
  1. Manganese dioxide, MnO_2.
     (a) It is an important oxidizing agent.
     (b) Used as a drier in paint oils, for decolorization of glass, and the construction of dry cells.
     (c) As a catalyst in numerous inorganic reactions, *e.g.*, the preparation of oxygen from potassium chlorate.
  2. Potassium permanganate, $KMnO_4$.
     (a) Used as a disinfectant, oxidizing agent, and as a volumetric reagent.

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- Valence Changes of Manganese.
    1. Mn^{++} + vigorous oxidizing agents (alkaline solution) → MnO_4^{--}.
    2. MnO_4^{--} (in solution) + CO_2 → MnO_4^{-} .
    3. MnO_4^{--} + H_2S, H_2SO_3 and other reducing agents → Mn^{++}.
    4. Manganates are stable only under alkaline conditions, permanganates under neutral or acid conditions.
- Analytical Test.
    1. Potassium permanganate is the most widely used oxidizing reagent in volumetric analysis.
    2. Manganese compounds may be weighed as the pyrophosphate or dioxide.

XV.8. Copper

Introduction

- Copper was called "cuprum" by the Romans because it came from the island of Cyprus.
- It is the first member of Group IB of the periodic table.
- It is often classified with the noble metals (Ag, Hg and Au) because it is found free in nature, appears below hydrogen in the activity series, and has a similar atomic structure.
- Copper was known to the earliest races of mankind.

Occurrence

- Copper occurs native, especially in Michigan.
- It is found in complex oxides and sulfides.
    1. Cuprite, Cu_2O, and melaconite, CuO.
    2. Chalcopyrite, $CuFeS_2$; bornite, Cu_3FeS_3; chalcocite, Cu_2S; and indigo copper, CuS.
- It is present as silicates and basic carbonates..
    1. Malachite, $Cu_2(OH)_2CO_3$, and azurite, $Cu_2(OH)_2(CO_3)_2$, $Cu(OH)_2 \cdot 2CuCO_3$.
- The United States produces two-thirds of the world's output.
    1. Leading producers are Arizona, Montana, Utah, Nevada, Colorado, and Michigan.
    2. Foreign producers are Mexico, Spain, Japan, Cuba, Australia, Chile, and the Belgian Congo.
    3. Butte, Montana, alone has a production equal to any two foreign countries combined.

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Metallurgy

- Smelting Process.

1. The ore is concentrated by *froth-flotation*.
   (a) A pine oil or mineral oil is mixed with the finely ground ore in water.
   (b) Air is blown through the suspension.
   (c) The ore particles rise to the surface with the air bubbles.
   (d) The gangue settles to the bottom.
   (e) Ninety per cent of the copper in a 2 per cent ore may be recovered by this method.
   (f) Over 60 million tons of copper ore are thus treated annually in the United States.
2. The concentrates are roasted to remove a portion of the sulfur.
3. The roasted concentrates are then melted in a reverberatory furnace in the presence of a silicious flux, and form a "matte."
   (a) Here the calcium, magnesium, aluminium, and iron enter the slag.
   (b) The slag is tapped from the furnace and discarded.
   (c) Gold, silver, and nickel enter the matte.
   (d) Zinc, lead, antimony, and arsenic are removed as fumes.
4. The fused matte is transferred to a copper converter, a silicious flux is added, and air is blown through it.
   (a) The remaining lead and iron enter the slag.
   (b) The remaining sulfur is oxidized.
   (c) "Blister copper" remains.
5. The blister copper is further purified by oxidation in a refining furnace.
   (a) Most impurities, except gold, silver, and platinum, are oxidized and slagged off.
6. The traces (3.5%) of cuprous oxide are now reduced by introducing green wood.
7. The rafined copper is then cast into anodes.
8. Almost all industrial copper is then purified (99.8%) by electrolysis.
   (a) The electrolyte is a solution of copper sulfate and sulfuric acid.
   (b) The copper plates on the cathode.
   (c) The silver and gold are collected as fine sludge or anode mud.

- The Leaching Process.

1. This method can be used only with oxide or carbonate ores.
2. The ore is extracted with sulfuric acid.
3. The copper is recovered by precipitation with metallic iron or by electrolysis.

Physical Properties

- Copper is reddish, bright, lustrous metal.

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- Atomic weight, 63.54. Atomic number, 29.
- Melting point, 1 083°C. Boiling point, 2 301°C.
- Specific gravity, 8.92.
- Copper is very malleable, ductile, and has high resistance to corrosion.
- Copper is a good conductor of heat and electricity.

Chemical Properties

- Valence, positive 1 (cuprous), and 2 (cupric).
- Copper is a typical heavy metal.
- Solutions of its salts react acid due to hydrolysis.
- Copper forms insoluble oxides, hydroxides, carbonates, phosphates, and oxalates.
- Copper forms numerous soluble complexes. For example, $Cu(NH_3)_4SO_4$, $Cu(CN)_2Cl$, and $KCu(CN)_2$.
- Metallic copper reacts with oxidizing acids only.

$$3\ Cu + HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

$$Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2\ H_2O$$

$$Cu + H_2SO_4 \xrightarrow{100°C} Cu_2S + CuSO_4 + H_2O$$

- Copper, when heated, combines with oxygen, sulfur, or the halogens.

$$2\ Cu + O_2 \rightarrow 2\ CuO$$

$$Cu + S \rightarrow CuS$$

$$Cu + Cl_2 \rightarrow CuCl_2$$

- Moist air converts copper into a basic carbonate.

$$2\ Cu + O_2 + CO_2 + H_2O \rightarrow Cu_2(OH)_2CO_3$$

$$Cu + O_2 + SO_2 + H_2O \rightarrow Cu(SO_4)\cdot 3Cu(OH)_2$$

Uses

- Copper is used for roofing, covering for ships'bottoms, lining and tubing in kettles, etc.
- Copper is used as a conductor in the electrical industry.
- It is used in the electrotyping process of printing books and illustrations.

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Copper Compounds

⇒ Copper oxide, CuO.

1. It is prepared by heating metallic copper in air.
2. It is an important oxidizing agent.

⇒ Copper sulfate (Blue vitriol), $CuSO_4 \cdot 5H_2O$.

1. It is prepared by the action of dilute sulfuric acid on copper in the presence of air.
2. It is used in batteries, copper refining, electroplating, calico printing, destruction of algae in water, preparation of *Bordeau Mixture* [$Ca(OH)_2 + CuSO_4$], Fehling's solution and other copper compounds.

Analytical Test

- Ammonium hydroxide in excess produces an intense blue color with cupric salts, due to the formation of the $Cu(NH_3)_4^{++}$ ion.
- Potassium ferrocyanide, $K_4Fe(CN)_6$, produces a dark red precipitate of $Cu_2Fe(CN)_6$ with cupric salts in neutral or faintly acid solution.
- Potassium iodide reacts with cupric salts to form cuprous iodide and iodine.

$$2\ CuSO_4 + 4\ KI \rightarrow 2\ CuI + 2\ K_2SO_4 + I_2$$

XV.9 Silver and gold

XV.9.1. Silver

- Introduction.
  1. Silver has been known since pre-Christian times.
  2. The symbol for silver is derived from the Latin word "argentum."
- Occurrence.
  1. Silver often occurs in association with gold (Electrum).
  2. Silver sulfide (argentite), Ag_2S, and silver chloride (horn silver), AgCl, are occasionally found.
  3. Silver is most frequently associated with copper and lead sulfides.
     (a) Silver is recovered from the anode mud in copper refining.
     (b) The Parke's process of refining lead produces considerable silver.
  4. The principal producers are the United States, Mexico, Spain, South America, and Japan.
- Metallurgy.
  1. Silver is recovered from copper refining.
  2. The Parke's process recovers silver from lead ores.

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(a) Molten zinc is only slightly soluble in molten lead.

(b) Molten zinc is used (0.8 to 1.5%) to extract the silver present.

(c) The zinc is removed from the silver by distillation.

3. The extraction of pure silver is often accomplieshed by amalgamation with mercury.

(a) The silver chloride is converted to silver, *e.g.*,

$$AgCl + Hg \rightarrow Ag + HgCl$$

(b) The silver is recovered by distillation of the mercury from the amalgam.

4. Silver may be recovered by a leaching process.

(a) The solvents commonly used are water for silver sulfate (obtained by carefully roasting sulfides); concentrated brine or thiosulfates for chlorides; and cyanide solutions.

(b) The silver is precipitated by the use of zinc or aluminium from the cyanide solution.

- Physical Properties.

1. Silver is white, brilliant, and metallic.
2. Atomic weight, 107.870. Atomic number, 47.
3. Melting point, 960.5°C. Boiling point, 1 950°C.
4. Specific gravity, 10.50.
5. Silver is hard, very malleable, and ductile.

(a) The silver in a dime could be drawn into a wire more than a mile long.

6. It excels all other metals as a conductor of heat and electricity.

- Chemical Properties.

1. Valence, positive 1.
2. Silver undergoes no change in water or pure air.
3. When melted, it absorbs 22 times its volume of oxygen, which it again expels on cooling.
4. It reacts with sulfur and sulfur compounds.

$$2\ Ag + S \rightarrow Ag_2S$$

$$2\ Ag + H_2S \rightarrow Ag_2S + H_2$$

(a) Foods rich in sulfur as egg yolks and mustard tarnish silverware.

5. Silver reacts with hot oxidizing acids.

$$6\ Ag + 8\ HNO_3 \rightarrow 6\ AgNO_3 + 4\ H_2O + 2\ NO$$

$$2\ Ag + 2\ H_2SO_4 \rightarrow Ag_2SO_4 + 2\ H_2O + SO_2$$

6. Silver halides, except AgF, are insoluble in water.
7. Silver salts form soluble complexes with an excess of NH_4OH and KCN, *e.g.*, $Ag(NH_3)_2Cl$ and $KAg(CN)_2$.

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8. Silver oxide is slightly soluble in water forming an alkaline solution.

$$Ag_2O + H_2O \leftrightarrow 2\ AgOH$$

- Uses.
  1. Silver is used for coinage, jewelry, and decorative purposes.
     (a) Sterling silver is 92.5% pure silver.
  2. Most modern morrors are plated with metallic silver.
  3. The silver halides are used in photography.
  4. Metallic articles are frequently plated with silver, as tableware.
- Compounds of Silver.
  1. Silver nitrate (Lunar caustic), $AgNO_3$.
     (a) It is prepared by the action of nitric acid on metallic silver.
     (b) It is used to prepare other silver compounds.
     (c) It is used in medicine and in certain indelible inks.
  2. Silver chloride, AgCl, silver bromide, AgBr, and siver iodide, AgI.
     (a) These silver salts are used extensively in photography.
     (b) They are prepared by double decompositions.

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl \downarrow$$

$$KBr + AgNO_3 \rightarrow KNO_3 + AgBr \downarrow$$

$$KI + AgNO_3 \rightarrow KNO_3 + AgI \downarrow$$

- Analytical Test.
  1. The presence of silver in solution is shown by the addition of a soluble chloride. A curdy white precipitate of AgCl is produced which is insoluble in dilute nitric acid, but is soluble in ammonium hydroxide.

XV.9.2. Photography

- Sixteenth century alchemists noticed that silver halides darkened on exposure to light.
- In 1800 Wedgood produced the first photograph.
- In 1839 Daguerre made permanent photographs.
- Modern photographic processes involve five major steps.
  1. The *film* is a plate of glass or sheet of celluloid coated with gelatin and colloidal silver bromide or silver iodide.
  2. The *exposure* is made with a camera, which initiates a partial reduction of the silver halides in the film, or plate producing a "latent" image.

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$$2\ AgBr + (light) \rightarrow Ag_2Br + Br \qquad \text{or}$$

$$2\ AgBr + (light) \rightarrow 2\ Ag + Br_2$$

3. The *development* is carried out in an alkaline solution of some organic reducing agent, producing a negative.

$$AgBr + Developer \rightarrow Ag + Br^- + Oxidized\ devepoler$$

4. The negative is then *fixed* in a solution of sodium hyposulfite (hypo) where the excess silver halide is dissolved and removed. The negative is then throughly washed.

$$AgBr + Na_2S_2O_3 \rightarrow NaAgS_2O_3 + NaBr$$

5. *Printing* and *toning* are then used to produce the negative of the negative or positive print.
   (a) This consists of a repetition of the previous operations except that a suspension of silver halides in gelatin on paper is used and the exposure is made by contact with the negative.
   (b) Special tones are produced by immersing the print in gold or platinum solutions.

XV.9.3. Gold

- Introduction.
  1. Gold has been valued highly from earliest times.
  2. The symbol for gold is derived from the Latin word, "aurum" which means "shining dawn."
- Occurrence.
  1. Gold is generally found in the free state, as grains or nuggets.
  2. Gold is sometimes associated with tellurium and lead in Colorado deposits.
  3. The leading producers are the Western United States, South Africa, Alaska, and Canada.
- Metallurgy.
  1. Because of its great density, gold is often recovered by panning or hydraulic mining.
  2. Most gold is extracted today by the use of sodium cyanide.

$$4\ Au + 8\ NaCN + 2\ H_2O + O_2 \rightarrow 4\ NaOH + 4\ NaAu(CN)_2$$

   (a) The gold is subsequently precipitated with metallic zinc.
  3. A portion of the gold is recovered by amalgamation with mercury.
- Physical Properties.
  1. Gold is soft, heavy, a beautiful yellow metal.
  2. Atomic weight, 196.967. Atomic number, 79.
  3. Melting point, 1 063°C. Boiling point, 2 600°C.
  4. Specific gravity, 19.32 at 17.5°C.

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5. It is the most malleable and ductile of all the metals.
6. It is a good conductor of heat and electricity.

- Chemical Properties.
  1. Valence, positive 1 and 3.
  2. Metallic gold does not corrode in air or react with inorganic acids.
  3. It unites with the free halogens and dissolves in aqua regia.
  4. It is soluble in sodium cyanide solution.
- Uses.
  1. Gold is used for coinage and jewelry.
     (a) By carats of gold is meant the twenty-fourths.
  2. Gold is used for gold lettering.
  3. Gold is used in dentistry.
- Compounds of Gold.
  1. Potassium aurocyanide, $KAu(CN)_2$ and potassium auricyanide, $KAu(CN)_4$, are used in gold plating baths.
  2. Chloroauric acid, $HAuCl_4$, is used for toning photographs.
- Analytical Test.
  1. A solution of stannous chloride produces a red coloration of colloidal gold when added to auric gold.
  2. Gold ores are usually analyzed by the fire assay method.

XV.10. Zinc, cadmium, and mercury

XV.10.1. Zinc, Zn

- Occurrence.
  1. Zinc sulfide (Sphalerite, "Black jack," or Zinc blende), ZnS.
  2. Zinc orthosilicate (Calamine), Zn_2SiO_4.
  3. Zinc carbonate (Smithsonite), $ZnCO_3$.
  4. Franklinite, $ZnFe_2O_4$.
  5. Zinc oxide (Zincite), ZnO.
  6. Zinc is commonly associated with lead and cadmium.
  7. Important producing states are Oklahoma, Missouri, New Jersey, Montana, Idaho, Utah, Colorado, and Kansas.

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- Metallurgy.
  1. The concentrated ore is roasted to remove sulfur and arsenic.

$$2\ ZnS + 3\ O_2 \xrightarrow{\Delta} 2\ ZnO + 2\ SO_2$$

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

  2. The zinc oxide is then reduced with anthracite coal, *e.g.*,

$$ZnO + C \xrightarrow{\Delta} Zn + CO$$

  3. The reduced zinc is purified by distillation.
  4. Zinc is sometimes purified by electrolysis.

- Physical Properties.
  1. Zinc is bluish-white, brittle metal.
  2. Atomic weight, 65.37. Atomic number, 30.
  3. Melting point, 419.4°C. Boiling point, 907°C.
  4. Specific gravity, 7.14 at 20°C.
  5. It is a fair conductor of electricity.
  6. It is malleable and ductilebetween 100°C and 150°C.
  7. Zinc is marketed as "zinc dust" or "spelter".

- Chemical Properties.
  1. Valence, positive 2.
  2. Zinc oxidizes readily in air but soon becomes coated with a protective layer of basic carbonate.
  3. Zinc burns with a blue flame.

$$Zn + O_2 \xrightarrow{\Delta} 2\ ZnO$$

  4. Zinc, because of its amphoteric nature, reacts with both acids and bases liberating hydrogen, *e.g.*,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \uparrow$$

$$Zn + 2\ NaOH \rightarrow Na_2ZnO_2 + H_2 \uparrow$$

  5. Zinc combines directly with sulfur and the halogens, *e.g.*,

$$Zn + S \rightarrow ZnS$$

$$Zn + Cl_2 \rightarrow ZnCl_2$$

  6. Zinc forms soluble complexes with ammonia.

$$Zn(NH_3)_4SO_4$$

  7. All zinc salts are poisonous.

- Uses.
  1. Zinc dust in an important reducing agent in the preparation of dyestuffs, synthetic drugs and perfumes.

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2. Zinc is used in precipitating gold and silver in the cyanide process.
3. Zinc is used in galvanizing and sherardizing steel.
4. Mettalic zinc is used for roofing and gutter-pipe.
5. Mettalic zinc is used in some alloys, *e.g.*, brass.
6. Zinc metal is used as the cathode container in making "dry cells."

- Compounds of Zinc.

1. Zinc Oxide (Zinc white), ZnO.

(a) Zinc oxide is produced by burning metallic zinc.

(b) It is used extensively as a paint pigment.

(1°) Zinc oxide, unlike white lead, is not darkened on exposure to sulfur compounds.

(c) It is used as a filler in automobile tires.

(d) Large quantities are used in the manufacture of oilcloth, enamels, glazes, and laboratory glassware.

2. Zinc chloride, $ZnCl_2$.

(a) A solution of zinc chloride is used in treating railroad ties to retard decay.

(b) Zinc chloride solution is used in the preparation of vulcanized fiber and waterproof paper.

(c) It is used as a soldering flux.

3. Zinc sulfate, $ZnSO_4$.

(a) Zinc sulfate solution is used as a mordant in cotton printing.

(b) It is used to fill pores in cement and plaster before painting.

(c) It is used as an antiseptic in glue solutions.

4. Lithopone ($BaSO_4 + ZnS$).

(a) It is prepared by double decomposition.

$$ZnSO_4 + BaS \rightarrow BaSO_4 \downarrow + ZnS \downarrow$$

(b) Lithapone is used extensively for interior white paint.

- Analytical Test.

1. Zinc sulfide, ZnS, precipitates with H_2S in neutral or alkaline solutions.
2. Potassium ferrocyanide produces a white precipitate of $Zn_2Fe(CN)_6$ with zinc salts.
3. Zinc compounds when fused on charcoal with sodium carbonate and a solution of cobalt nitrate produce a green color. (Reinmann's green.)

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XV.10.2. Cadmium, Cd

- Occurrence.
    1. Traces of cadmium occur in almost all zinc ores.
    2. It is separated by fractional distillation, solution in sulfuric acid and electrolysis.
- Physical Properties.
    1. Cadmium is a soft, bluish-white, ductile metal.
    2. Atomic weight, 112.40. Atomic number, 48.
    3. Melting point, 320.9°C. Boiling point, 778°C.
    4. Specific gravity, 8.65 at 20°C.
- Chemical Properties.
    1. Valence, positive 2.
    2. Cadmium salts form soluble complexes with ammonium hydroxide, *e.g.*, $Cd(NH_3)_4SO_4$.
- Uses.
    1. Cadmium is used principally in making low melting alloys. For example, Wood's metal.
    2. Sheet steel is often electroplated with cadmium. (Udylitte process.)
    3. Cadmium sulfide, CdS, is a lemon-yellow paint pigment.
- Analytical Test.

1. Yellow cadmium sulfide precipitates with H_2S from soluble cadmium salts in acid solution.

XV.10.3. Mercury, Hg

- Introduction.
    1. Mercury is named after the planet by the same name.
    2. It derives its symbol from the Latin word, "Hydrargyrum."
    3. Mercury was known to the ancient Chinese and Hindus.
    4. It has been found in Egyptian tombs of 1500 B.C.
    5. It is the only metal that exist as a liquid at ordinary temperatures.
    6. It is often to as, "quicksilver."
- Occurrence.
    1. The principal ore is *cinnabar*, HgS.
    2. Important producers of mercury are California, Spain, and Austria.
- Metallurgy.
    1. Cinnabar is roasted in a current of air and the mercury is condensed.

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$$HgS + O_2 \xrightarrow{\Delta} Hg + SO_2$$

- Physical Properties.
  1. Mercury is a heavy, silver-white, shining liquid.
  2. Atomic weight, 200.59. Atomic number, 80.
  3. Melting point, -38.87°C. Boiling point, 365.9°C.
  4. Specific gravity, 13.595 at 4°C.
  5. It is a fair conductor of heat and electricity.
  6. It has a regular coefficient of expansion.
- Chemical Properties.
  1. Valence, positive 1 (mercurous), and positive 2 (mercuric).
  2. Mercury tarnishes slowly in air unless heated to near its boiling point.

$$2\ Hg + O_2 \xrightarrow{\Delta} 2\ HgO$$

  3. Mercury, dissolves many other metals as Au, Ag, Na, and K, forming amalgams.
  4. Mercuric salts reacts with ammonia forming ammonobasic mercuric salts, *e.g.*,

$$HgCl_2 + 2\ NH_3 \rightarrow Hg(NH_2)Cl + NH_4Cl$$

  5. Mercury combines with the halogens.

$$Hg + Cl_2 \rightarrow HgCl_2$$

  6. Mercury combines with sulfur at room temperature.

$$Hg + S \rightarrow HgS$$

  7. Mercury reacts with nitric and hot concentrated sulfuric acid.

$$3\ Hg + 8\ HNO_3 \rightarrow 3\ Hg(NO_3)_2 + 4\ H_2O + 2\ NO$$

$$Hg + 2\ H_2SO_4 \rightarrow HgSO_4 + 2\ H_2O + SO_2$$

  8. All soluble mercury compounds are extremely poisonous.
- Uses.
  1. Mercury is used in thermometers, barometers, and high-vacuum air pumps.
  2. It is used in the amalgamation process for extracting gold and silver from their ores.
  3. It is used in preparing dental alloys.
  4. The telescope at Mount Wilson observatory is ballanced in metallic mercury.
  5. Al alloy of sodium and mercury (amalgam) is an important reducing agent.
  6. The mercury arc lamp produces a blue light, rich in ultra-violet rays.
  7. Mercury arc rectifiers are used in charging batteries.
  8. Mercury vapor engines are coming into use and seem to offer interesting possibilities for increased efficiency.
- Compounds of Mercury.

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1. Mercuric chloride (corrosive sublimate), $HgCl_2$.

   (a) It is a white, soluble, poisonous salt and is a powerful antiseptic.

2. Mercuric oxide (red precipitate), HgO.

   (a) It is prepared by heating mercury in air, and again releases its oxygen when heated to a higher temperature.

   (b) It is used as a paint pigment for ships.

3. Mercuric sulfide (vermilion), HgS.

   (a) It is used as a paint pigment.

4. Mercurous chloride (calomel), HgCl or Hg_2Cl_2.

   (a) It is used in medicine.

5. Mercurous sulfate, Hg_2SO_4.

   (a) Mercurous sulfate is used in the preparation of standard cells.

- Analytical Test.

1. Mercurous salts produce a white precipitate with a soluble chloride. This mercurous chloride darkens on the addition of ammonia.

$$Hg + Cl \rightarrow HgCl \downarrow$$

$$2\ HgCl + 2\ NH_3 \rightarrow Hg(NH_2)Cl + Hg + NH_4Cl$$

2. Mercuric salts form insoluble, HgS, with H_2S. The HgS is insoluble in nitric acid and ammonium polysulfide.

3. Stannous chloride solution produces a white precipitate of mercury.

$$HgCl_2 + SnCl_2 \rightarrow SnCl_4 + 2\ HgCl \downarrow$$

$$HgCl_2 + SnCl_2 \rightarrow SnCl_4 + Hg \downarrow$$

4. A copper wire dipped in an acid solution of a mercury salt soon becomes coated with a gray or silvery deposit of mercury.

5. Mercury may be precipitated and weighed as the sulfide.

XV.11. Tin and lead

XV.11.1. Introduction

- Tin and lead appear of Group IVB of the periodic table.
- Deposits of tin in Conwall, England, were worked by the Phoenicians as early as 1000 B.C.
- The Romans used lead for water coduits in ancient times. Lead is mentioned in Exodus.

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XV.11.2. Tin

- Occurrence.
  1. *Casserite or tinstone*, SnO_2, is the principal source of tin.
  2. Minor deposits of sulfides are known.
  3. The Malay States, Bolivia, the East Indes, China, and Alaska are important producers.
- Metallurgy.
  1. The ore is crushed and concentrated by washing with water.
  2. The concentrated ore is then roasted to remove sulfur and arsenic.
  3. It is then reduced with coal in a reverberatory furnace.

$$SnO_2 + C \rightarrow Sn + CO_2$$

- Physical Properties.
  1. Tin is a silver white, malleable, ductile, crystalline metal.
  2. Atomic weight, 118.69. Atomic number, 50.
  3. Melting point, 231.9°C. Boiling point, 2 270°C.
  4. Specific gravity; gray, 5.75; rhombic, 6.55; and tetragonal, 7.31 at 20°C.
  5. Tin exists in three allotropical forms.

(a) Gray tin $\xleftrightarrow{18°C}$ Tetragonal tin $\xleftrightarrow{170°C}$ Rhombic tin

(b) Both gray and rhombic tin are brittle and are easily powdered.

- Chemical Properties.
  1. Valence, positive 2 (stannous), and positive 4 (stannic).
  2. Tin lies just above hydrogen in the activity series.
  3. Molten tin reacts with steam liberating hydrogen.

$$2\ Sn + 2\ H_2O \rightarrow SnO_2 + 2\ H_2$$

  4. Metallic tin does not tarnish in moist air in years.
  5. Tin reacts with the common acids.

$$Sn + 2\ HCl \rightarrow SnCl_2 + H_2$$

$$3\ Sn + 4\ HNO_3 + H_2O \rightarrow 3\ (SnO_2 \cdot H_2O) + 4\ NO \qquad \text{or}$$

$$Sn + 4\ HNO_3 \rightarrow SnO_2 \cdot H_2O + 4\ NO_2 + H_2O$$

  6. Stannous and stannic hydroxides are amphoteric forming stannites and stannates.

$$Sn(OH)_2 + 2\ HCl \rightarrow SnCl_2 + 2\ H_2O$$

$$Sn(OH)_2 + 2\ NaOH \rightarrow Na_2SnO_2 + 2\ H_2O$$

- Uses.

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1. "Tin cans" are made from tin-plated sheet steel.
2. Tin is used in alloys, *e.g.*, solder, babbitt, and bronze.
3. Tin foil is used to wrap candy, tobacco, tea, and food products.

- Compounds of Tin.
  1. Tin forms two oxides, SnO and SnO_2, and two series of salts.
  2. Stannic oxide, SnO_2.
     (a) It is prepared by igniting metastannic acid, H_2SnO_3, which in turn is prepared by the action of nitric acid on tin.
     (b) It is used to produce brilliant white enamels for kitchenware and earthenware.
  3. Stannous chloride, $SnCl_2 \cdot H_2O$.
     (a) It is used as a mordant in calico printing.
     (b) It is an important analytical reducing agent.
  4. Stannic chloride, $SnCl_4$.
     (a) It is a colorless fuming liquid.
     (b) It is used as a mordant and in fireproofing cotton.

- Analytical Test.
  1. Tin is precipitated as, SnS or SnS_2, from acid solution.
  2. Tin, in the stannous condition, reduces mercuric chloride and bismuth hydroxide producing dark precipitates of the free metals in each case.

XV.11.3. Lead

- Occurrence.
  1. The principal ore is galena, PbS.
  2. Smaller deposits, near galena, of sulfate, carbonate, and chromate are usually encountered.
  3. Important producers are Missouri, Idaho, Utah, and Oklahoma, the United States producing 35% of the total. The United States and Mexico produce 50% of the world's supply.

- Metallurgy.
  1. Lead sulfide is partially roasted at a low temperature in a reverberatory furnace with a limited supply of air.

$$2\ PbS + 3\ O_2 \xrightarrow{\Delta} 2\ PbO + 2\ SO_2$$

$$PbS + 2\ O_2 \xrightarrow{\Delta} PbSO_4$$

  2. The temperature is then raised and reduction follows.

$$PbS + 2\ PbO \xrightarrow{\Delta} 3\ Pb + SO_2$$

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$$PbS + PbSO_4 \xrightarrow{\Delta} 2\,Pb + 2\,SO_2$$

3. The silver is removed by extracting with Zinc (0.8 to 1.5%) in a molten condition. (Parke's process.)
4. The desilverized lead is cast into anodes and electrolyzed in a solution of $PbSiF_6$ in the presence of a little gelatin. (Betts' process.)

- Physical Properties.
  1. Lead is a soft, gray, metal with low tensile strength.
  2. Atomic weight, 207.19. Atomic number, 82.
  3. Melting point, 327.5°C. Boiling point, 1 620°C.
  4. Specific gravity, 11.35.
  5. Lead is highly malleable, is ductile, and is a poor conductor of electricity.
- Chemical Properties.
  1. Valence, positive 1, 2, and 4.
  2. Lead oxidizes slowly in air, for a coating of basic carbonate soon protects it from further oxidation.
  3. It is slowly attacked by sulfuric acid due to a protective coating of insoluble lead sulfate that soon forms.
  4. Lead reacts with nitric acid.

$$3\,Pb + 8\,HNO_3 \rightarrow 3\,Pb(NO_3)_2 + 4\,H_2O + 2\,NO$$

- Uses.
  1. It is used for pipe and containers for corrosive liquids.
  2. It is used in many alloys. For example, solder, type metal, antifriction alloys, and shot.
  3. Lead binds bits of colored glass together in decorative windows.
  4. Telephone cables and storage batteries use large amounts of lead.
  5. Lead is used for preparing "white lead."
- Compounds of Lead.
  1. Lead monoxide (Litharge), PbO.
     (a) It is prepared by heating lead at 550°C.
     (b) It is used in refining petroleum, making optical glass, enamels, glazes, varnish-driers, vulcanizing rubber, and for making glass and stone cement.
  2. Red lead (Minium), Pb_3O_4.
     (a) It is prepared by heating litharge to 500°C for some time.
     (b) It is used as a paint pigment, for making flintglass, caulking joints in steam and gas pipes, and is an important oxidizing agent.
  3. Lead dioxide (lead peroxide), PbO_2.

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(a) It is prepared by oxidizing a lead salt.

$$PbCl_2 + CaOCl_2 + H_2O \rightarrow PbO_2 + CaCl_2 + 2\ HCl$$

$$Pb_3O_4 + 4\ HNO_3 \rightarrow 2\ Pb(NO_3)_2 + PbO_2 + 2\ H_2O$$

(b) It is used in lead storage batteries as an oxidizing agent.

4. White lead, $Pb(OH)_2 \cdot 2PbCO_3$.

(a) This is an important paint pigment.

(b) Two methods of manufacture are in general use.

(1°) Dutch process.

a. Perforated pieces of lead are piled in pots with acetic acid and tanbark.

b. Lead acetate is formed and in then converted to the basic carbonate by the carbon dioxide from the tanbark.

c. The process requires three months.

(2°) French or Carter process.

a. Granulated lead is exposed to the action of steam, carbon dioxide, and acetic acid vapor, for a week or more.

5. Lead acetate (Sugar of Lead), $Pb(C_2H_3O_2)_2$.

(a) It is prepared by dissolving litharge in acetic acid.

(b) It is used where a soluble lead salt is required.

(c) It is extremely poisonous.

6. Lead chromte (Chrome yellow), $PbCrO_4$.

(a) This is an imporatnt yellow paint pigment.

7. Lead arsenate, $Pb_3(AsO_4)_2$.

(a) This is an important insecticide.

- Analytical Test.

1. Any compound of lead, when fused with sodium carbonate on charcoal, produces a bead of metallic lead, surrounded by a ring of litharge, red when hot, and yellow when cold.
2. Hydrogen sulfide in acid solution precipitates black lead sulfide, PbS.
3. Soluble iodides precipitate yellow, PbI_2.
4. Soluble chlorides precipitate white lead chloride, $PbCl_2$, which is soluble in hot water.
5. Potassium chromate or dichromate precipitates yellow lead chromate, $PbCrO_4$.
6. Sulfuric acid slowly precipitates white lead sulfate, $PbSO_4$, which is soluble in acetate solutions.

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XV.12. THE PLATINUM METALS

XV.12.1. Introduction

- The platinum group of metals contains six rare metals, ruthenium, (Ru); rhodium, (Rh); palladium, (Pd); osmium, (Os); iridium, (Ir); and platinum, (Pt).
- These elements appear in Group VIII of the periodic table and constitute the second and third transition groups.
- They appear native and together in nuggents and grains in alluvial sands.
- The chief deposits are in the Ural Mountains of Russia, Colombia, the United States, and the Transvaal.
- These six elements show strikingly similar physical and chemical properties.
- They behave as typical noble metals and have great tendencies to form complex ions.
- They all possess a silvery luster, are quite dense, and have high melting points.
- Alltheir compounds are relatively unstable to heat.
- They all show a valence of four, and each exhibits other valences.

XV.12.2. Platinum

- Plarinum is the most abundant and important of the six metals.
- Crude platinum is purified by dissolving the ore in aqua regia, evaporation of the acid and subsequent addition of hydrochloric acid and NH_4Cl. The precipitate of $(NH_4)_2PtCl_6$ is converted to spongy platinum by ignition.
- Metallic platinum is used in dentistry, the electrical industry, in jewelry, and as a catalyst, and for laboratory apparatus.

  1. Catalytic uses involve the manufacture of sulfuric acid, ammonia, and nitric acid.
- Platinum is extremely resistant to all acids, solutions of salts and alkalies, but not to aqua regia or fused alkalies, a smoky flame, or lead, arsenic or phosphorus compounds in presence of reducing agents.

XV.12.3. Properties and Uses of the Other Platinum Metals

⇒ Rhutenium, Ru.

1. Rhutenium resembles silver in many respects.

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2. Ruthenium displays the unusual valence of 8, among several other valences.
3. Its name suggests its source, "Ruthenia or Russia."

⇒ Rhodium, Rh.

1. Its name is derived from the Greek word, "rhodon," meaning, "rose."
2. The salts of rhodium form red solutions.
3. It is alloyed with platinum to make thermojunctions in pyrometers.

⇒ Palladium, Pd.

1. Palladium resembles silver in many respects.
2. Finely derived palladium is often used as a catalyst where the addition of oxygen is involved. One volume of palladium will absorb 900 volumes of gas.
3. A palladium-gold alloy (Palau) is used as a substitute for platinum in making laboratory apparatus.

⇒ Osmium, Os.

1. Osmium resembles gold somewhat in properties.
2. Osmium tetroxide, OsO_4, is used to strain fats in microscopical work.
3. It is alloyed with platinum to render hardness.
4. Osmium displays the unusual valence of 8, among several other valences.
5. It is the heaviest known form of matter, with a specific gravity of 22.48.

⇒ Iridium, Ir.

1. It is alloyed with platinum up to 10% to make laboratory apparatus harder.
2. Iridium alloys are used for fountain pen points.
3. It is used for standard weights and measures when alloyed with platinum.

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XVI. CHEMISTRY OF THE NONTRANSITION ELEMENTS

-The non-metals-

XVI.1 Chlorine and hydrogen chloride

XVI.1.1. Introduction

- In 1774 the Swedish chemist, Scheele, obtained a greenish yellow gas by heating hydrochloric acid with a number of oxidizing agents.

1. He believed that this new gas contained oxygen in combination with some other element.
2. Some forty years later Sir Humphry Davy, proved that this gas contained no oxygen, since no carbon dioxide was obtained when it was heated with white hot carbon, or water when it was heated with hydrogen.
3. Sir Humphry Davy gave this new gas the name of chlorine, meaning yellowing green.

XVI.1.2. Occurrence

- Chlorine never occurs free in nature.
- The ocean contains 2.8% of common salt (NaCl) and 0.8% of other matallic chlorides.
- Numerous salt lakes, salt wells, and salt beds are found in all parts of the world, *e.g.*,
  1. Great Salt Lake and Dead Sea.
  2. Michigan, Kansas, New York, and Ohio are leading producers.
  3. Deposits of Stassfurt, Germany, and Alsace, France.
- In combination with hydrogen as hydrogen chloride in gases from volcanoes.
  1. Some streams of the slopes of the Andes contain so much dissolved hydrogen chloride that fish can not live in them.
- Hydrochloric acid (HCl) is secreted by the glands of the stomach and is an essential componen of gastric juice. (0.2 to 0.4%.)

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XVI.1.3. Preparation

- Laboratory Methods.

1. Action of an oxidizing agent on hydrochloric acid.

(a) $4\ HCl + MnO_2 \rightarrow MnCl_2 + 2\ H_2O + Cl_2$

(b) $14\ HCl + K_2Cr_2O_7 \rightarrow 2\ KCl + 2\ CrCl_3 + 7\ H_2O + 3\ Cl_2$

2. By action of acid on bleaching powder.

(a) $CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

- Commercial Methods.

1. Electrolysis of brine (NaCl).

(a) $2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + H_2 + Cl_2$

2. Deacon's Process (not used extensively today).

(a) $4\ HCl + O_2 \xrightarrow{450^\circ} 2\ H_2O + Cl_2$

XVI.1.4. Physical Properties

- Atomic weight, 35.453. Atomic number, 17.
- Chlorine is a yellowish green gas, condensable to a yellow liquid.
- It has an irritating odor, and is very poisonous.
- Boiling point, -34.6°C. Freezing point, -101.6°C.
- Density, 3.214 g/l. About two and half time as heavy as air.
- Solubility in water, 310 cc in 100ml of water at 10°C. 177 cc in 100 ml of water at 30°C.

XVI.1.5. Chemical Properties

- Valence, negative 1, and positive 1, 3, 4, 5 and 7.
- Chlorine combines directly with metals, nonmetals, and hydrogen.

(a) $2\ Na + Cl_2 \rightarrow 2\ NaCl$

(b) $2\ Sb + 5\ Cl_2 \rightarrow 2\ SbCl_5$

(c) $2\ Hg + Cl_2 \rightarrow 2\ HgCl$, or $Hg + (\text{excess})\ Cl_2 \rightarrow HgCl_2$

(d) $2\ Au + (\text{moist})\ 3\ Cl_2 \rightarrow 2\ AuCl_3$

2. Non-metals.

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(a) $2\ P + 3\ Cl_2 \rightarrow 2\ PCl_3$, or $2\ P + 5\ Cl_2 \rightarrow 2\ PCl_5$

(b) $2\ S + Cl_2 \rightarrow S_2Cl_2$

3. Hydrogen (in sunlight with explosive violence).

(a) $H_2 + Cl_2 \rightarrow 2\ HCl$

- Chlorine dissolves in and reacts with water.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

- Chlorine reacts with many organic compounds.

$$C_2H_4 \text{ (ethylene)} + Cl_2 \rightarrow C_2H_4Cl_2 \text{ (ethylene dichloride)}$$

$$C_{10}H_{16} \text{ (Turpentine)} + 8\ Cl_2 \rightarrow 10\ C + 16\ HCl$$

- Chlorine reacts with alkalies and carbonates to form hypochlorites at room temperature.

$$Cl_2 + 2\ NaOH \rightarrow NaCl + NaOCl + H_2O$$

$$Cl_2 + Na_2CO_3 \rightarrow NaCl + NaOCl + CO_2$$

$$Cl_2 + CaO \rightarrow CaOCl_2 \text{ (Bleaching powder)}$$

- Free chlorine replaces bromine and iodine from their simple halides, *e.g.*,

$$2\ NaBr + Cl_2 \rightarrow 2\ NaCl + Br_2$$

$$2\ KI + Cl_2 \rightarrow 2\ KCl + I_2$$

- Chlorine serves as an oxidizing agent on many salts.

$$2\ FeCl_2 + Cl_2 \rightarrow 2\ FeCl_3$$

XVI.1.6. Uses

- Bleaching Wood Pulp.
  1. About two-thirds of the chlorine produced is used to bleach wood pulp for paper and rayon
- Bleaching Textiles.
  1. About one-fifth of the chlorine produced is used to bleach cotton and linen textiles.
- Laundry Bleach.
  1. Many commercial and home laundries use hypochlorite solutions for a bleach in washing clothes.
- For Bleaching Flour.
  1. Small amounts are used for bleaching flour in some instances.
- Purification of Drinking Water.

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1. One-tenth of the total production is used for the sterilization of drinking water.
2. This is perhaps the most practical, economical, and reliable method available today, and this use of chlorine is rapidly increasing.

- Organic Chemical Industry.
  1. Many important organic compounds are made today by the direct or indirect use of chlorine, such as chloroform, $CHCl_3$; carbon tetrachloride, Ccl_4; and ethylene dichloride, $C_2H_4Cl_2$.
- Inorganic Chemical Industry.
  1. Chlorine is used in the production of many important inorganic compounds such as hypochlorites, bleaching powder, chlorates, perchlorates, and sulfur monochloride.
- Extraction of Metals.
  1. Gold and tin are sometimes extracted from their ores by the use of chlorine.
- Warfare.

1.Most toxic "gases" used during World War I were volatile liquids that contained chlorine.

(a) Phosgene, $COCl_2$

(b) Mustard gas, $ClC_2H_2 \cdot S \cdot C_2H_4Cl$

(c) Tear gas (Chloropicrin), CCl_3NO_2

(d) Sneeze gas (Diphenyl chloroarsine), $(C_6H_5)_2AsCl$

XVI.1.7. Analytical Test

- Free chlorine gas can usually be recognized by its prominent physical properties and its ability to turn starch-iodide paper blue.
  1. Ozone has a similar effect on starch-iodide paper but ozone is a colorless gas.
- Chlorides form a white precipitate with silver nitrate ($AgNO_3$) which is insoluble in dilute nitric acid (HNO_3) and soluble in dilute ammonium hydroxide (NH_4OH).

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl \downarrow$$

$$HCl + AgNO_3 \rightarrow HNO_3 + AgCl \downarrow$$

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XVI.1.8. Hydrogen chloride

XVI.1.8.1. Preparation

- Action of non-volatile acid on metallic chloride.

$$H_2SO_4 + NaCl \xrightarrow{\Delta} NaHSO_4 + HCl \uparrow$$

$$NaHSO_4 + NaCl \xrightarrow{\Delta\Delta} Na_2SO_4 + HCl \uparrow$$

- By the direct union of hydrogen and chlorine under very carefully controlled conditions.

$$H_2 + Cl_2 \rightarrow 2\ HCl$$

- By the hydrolysis of the chlorides of phosphorus.

$$PCl_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HCl \uparrow$$

$$PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5\ HCl \uparrow$$

XVI.1.8.2. Physical Properties

- A colorless gas with a sharp, penetrating odor.
- About one-fourth heavier than air.
- Readily condensable to a liquid by application of pressure below 52.3°C.(the critical temperature)
- Dry hydrogen chloride is comparatively inert and does not conduct an electrical current.
- Dissolved in water it behaves as a typical strong acid.
- Very soluble in water, one volume of water dissolving over 300 volumes of hydrogen chloride.
- Hydrogen chloride forms a constant boiling solution with water. (20.24% HCl at 760mm pressure. Boiling point, 110°C.)

XVI.1.8.3. Chemical Properties

- Hydrogen chloride gas.

  1.Exposed to moist air it forms dense fumes due to its great solubility in water.

  2. It forms a white cloud with ammonia gas.

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$$HCl + NH_3 \rightarrow NH_4Cl$$

3. Dissolved in dry ether it reacts rapidly with zinc.

$$Zn + 2\ HCl \rightarrow ZnCl_2 + H_2$$

- Hydrochloric Acid (water solution of hydrogen chloride).

1. It reacts with active metals.

$$Mg + 2\ HCl \rightarrow MgCl_2 + H_2 \uparrow$$

$$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2 \uparrow$$

2. It reacts with carbonates.

$$Na_2CO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2O + CO_2 \uparrow$$

3. It reacts with sulfites.

$$Na_2SO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2O + SO_2 \uparrow$$

4. It reacts with bases.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

- It possesses many other typical properties of strong acids.

XVI.1.8.4. Uses

- Making ammonium chloride used in dry cells.
- Preparation of glucose from corn starch.
- Extracting glue from bones.
- Purifying boneblack.
- Cleaning metals before soldering or plating.

1. Soldering acid consists of a saturated solution of zinc chloride in dilute hydrochloric acid.

XVI.2. The halogens

XVI.2.1. Introduction

- The halogens, fluorine, chlorine, bromine, iodine, and astatine, appear in column seven of the periodic table, and hence have seven electrons in their valence shell.

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- They are a closely related family, showing a common valence and related physical and chemical properties.
- The name halogen means "salt former" and suggest something of their occurrence.

XVI.2.2. Discovery

- Fluorine was discovered in 1886 by Henri Moissan by electrolytic methods, and owes its name to its occurrence in the mineral, fluorite.
- Bromine was discovered in 1826 by Balard in the mother-liquor obtained after the crystallization of common salt by the evaporation of sea-water.
    1. It derives its name from the Greek word meaning, "a stench."
- Iodine was discovered independently by Davy and Gay-Lussac in 1812 in kelp residues after removal of the sodium carbonate.
    1. The name comes from the Greek word meaning, "violet colored."
- Astatine was discovered in 1940 by Corson, McKenzie and Segre by artificially bombarding bismuth with high energy alpha particles, accelerated in the Berkeley cyclotron.
    1. All the known isotopes are short-lived, the most stable having a half-life of only 7.5 hours.

XVI.2.3. Occurrence

- Fluorine. (0.1% of earth's crust.)
    1. In calcium fluoride, CaF_2, and cryolite, Na_3AlFe_6.
- Bromine. (0.001% of earth's crust.)
    1. In sodium bromide, NaBr, in the ocean, salt laken and salt beds of Stassfurt, Germany, and Michigan.
- Iodine. (0.001% of earth's crust.)
    1. Only traces in ocean water.
    2. Associated with Chile salpeter in the deposits of Chile, as sodium iodide, $NaIO_3$, and periodate, $NaIO_4$.

3. Brine from oil wells of southern California.

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XVI.2.4. Preparation

- Fluorine.

  1. By electrolysis of molten potassium hydrogen fluoride, KHF_2.

- Bromine.

  1. From mother-liquor by treatement with chlorine, aeration, absorption in sodium carbonate solution and subsequent treatement with acid. (Commercial method.)

$$2\ NaBr + Cl_2 \rightarrow 2\ NaCl + Br_2$$

$$3\ Br_2 + 3\ Na_2CO_3 \rightarrow NaBrO_3 + 5\ NaBr + 3\ CO_2$$

$$Na_2BrO_3 + 5\ NaBr + 3\ H_2SO_4 \rightarrow 3\ Na_2SO_4 + 3\ H_2O + 3\ Br_2$$

  2. By treating sea-water with chlorine and sulfuric acid, aeration, absorption in sodium carbonate solution, and subsequent treatement with acid and steam.

     (a) A huge plant of this type is in operation along the North Carolina coast, using over 1,000,000 tons of sea-water and producing about 15,000 pounds of bromine daily.

  3. By chemical oxidation of bromides with manganese dioxide, permanganates, or dichromates. (Laboratory method.)

$$2\ NaBr + 2\ H_2SO_4 + MnO_2 \xrightarrow{\Delta} MnSO_4 + Na_2SO_4 + 2\ H_2O + Br_2$$

  4. By replacement of bromine in bromides with chlorine. (Laboratory method.)

$$2\ NaBr + Cl_2 \rightarrow 2\ NaCl + Br_2$$

- Iodine.

  1. From California brines by adding a trace of acid with an oxidizing agent such as sodium nitrite. The free iodine is then removed by activated charcoal, extracted with caustic soda from which the iodine is obtained by use of an acid and oxidizing agent. (Commercial method.)

  2. By oxidation of iodides in acid solution. (Laboratory method.)

$$2\ KI + 2\ H_2SO_4 + MnO_2 \xrightarrow{\Delta} K_2SO_4 + MnSO_4 + 2\ H_2O + I_2$$

  3. By replacement of iodine in iodides with chlorine or bromine. (Laboratory method.)

$$2\ KI + Cl_2 \rightarrow 2\ KCl + I_2$$

$$2\ NaI + Br_2 \rightarrow 2\ NaBr + I_2$$

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XVI.2.5. Physical Properties

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Halogen	*Color and State*	*Atomic weight*	*Melting Point*	*Boiling Point*
Fluorine	Pale yellow gas	19.00	-233.0	-187.9
Chlorine	Greenish-yellow gas	35.453	-100.9	-34.0
Bromine	Dark red liquid	79.909	-7.2	58.8
Iodine	Purplish-black solid	126.90	113.5	184.4

- Liquid bromine produces serious, slow-healing burns.
- Iodine sublimes when heated.
- Fluorine reacts readily with water. Chlorine dissolves somewhat and reacts slowly with water. Bromine is less soluble in water, and iodine only very slightly soluble.

XVI.2.6. Chemical Properties

- Valence.
  1. Fluorine, negative 1.
  2. Chlorine, negative 1, and positive 1, 3, 4, 5, and 7.
  3. Bromine, negative 1, and positive 1, 3, 5, and 7.
  4. Iodine, negative 1, and positive 1, 3, 5, and 7.
- The halogens combine directly with hydrogen, forming halides, which behave as typical acids in solution.

$$H_2 + F_2 \xrightarrow{-250^\circ C} 2\,HF \text{ (Explosively).}$$

$$H_2 + Br_2 \xrightarrow{200^\circ C} 2\,HBr \text{ (A catalyst aids).}$$

$$H_2 + I_2 \xleftrightarrow{\Delta} 2\,HI \text{ (A catalyst is essential).}$$

- The halogens combine directly with most metals and many non-metals.

$$2\,Na + Cl_2 \rightarrow 2\,NaCl$$

$$Mg + Br_2 \rightarrow MgBr_2$$

$$2\,P + 3\,I_2 \rightarrow 2\,PI_3$$

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- Any halogen will replace another halogen with a greater atomic weight from binary compounds.

$$2\ NaBr + Cl_2 \rightarrow 2\ NaCl + Br_2$$

$$2\ KI + Br_2 \rightarrow 2\ KBr + I_2$$

- The free halogens, except fluorine, react with cold solutions of bases and carbonates to form halides and hypohalites, and with hot solutions they form halides and halate.

$$Cl_2 + 2\ NaOH \rightarrow NaCl + NaOCl + H_2O$$

$$Cl_2 + Na_2CO_3 \rightarrow NaCl + NaOCl + CO_2$$

$$3\ Cl_2 + 3\ Na_2CO_3 \xrightarrow{\Delta} 5\ NaCl + NaClO_3 + 3\ CO_2$$

$$3\ Br_2 + 6\ NaOH \xrightarrow{\Delta} 5\ NaBr + NaBrO_3 + 3\ H_2O$$

- The halogens are important oxidizing agents.

$$2\ FeCl_2 + Cl_2 \rightarrow 2\ FeCl_3$$

$$Cu + Br_2 \rightarrow CuBr_2$$

- The halogens combine or react with a number of inorganic compounds.

$$CO + Cl_2 \rightarrow COCl_2$$

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

$$H_2S + I_2 \rightarrow 2\ HI + S$$

$$H_2O + Br_2 \rightarrow HBr + HOBr$$

XVI.2.7. Uses

- Fluorine.
  1. Preparation of fluorine compounds only.
- Bromine.
  1. Preparation of dyestuffs, hypobromites and disinfectants.
  2. Medicine as bromides as heart depressants and nerve sedatives.
  3. Photography as silver bromide in the preparation of films, plates, and papers.
  4. Preparation of ethylene dibromide, $C_2H_4Br_2$, used in making tetraethyl lead, $(C_2H_5)_4Pb$, as an ant-knock for gasoline.
- Iodine.
  1. Medicine as tincture of iodine and iodoform, CHI_3.
  2. Photography as silver iodide in the preparation of films, plates, and papers.

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3. Necessary ingredient of human diet to prevent creatinism, and certain forms of goiter.

XVI.2.8. Analytical Tests

- Advantage is taken of the insolubility of silver chloride, bromide, and iodide in both the qualitative and quantitative determination of these halides.

1. Silver chloride is white, silver bromide pale yellow, and silver iodide lemon yellow.

- Bromides and iodides are also liberated by chlorine water and may be recognized by their characteristic colors after extraction with carbon disulfide, carbon tetrachloride, etc.
- Free chlorine, bromine, and iodine are liberated from their halides by treatement with sulfuric acid and manganese dioxide.
- Iodine produces a characteristic blue color with starch paste.
- Fluorides etch glass when treated with concentrated sulfuric acid.

XVI.2.9. Important Halogen Compounds

- Fluorine.

⇒ *Cryolite*, Na_3AlF_6, is used as a solvent in the electrolitic preparation of aluminium.

⇒ *Hydrogen fluoride* (hydrofluoric acid), HF, is used both as a gas and in solution to etch glass.

(a) It is prepared by the action of concentrated sulfuric acid on calcium fluoride.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ HF\ \uparrow$$

(b) Its action on glass and sand is due to the silicon dioxide present.

$$SiO_2 + 4\ HF \rightarrow SiF_4\ \uparrow + 2\ H_2O$$

⇒ *Sodium fluoride* is now added in small quantities to the water supplies of many cities.

(a) Traces of fluoride ion in drinking water appear to be essential to the normal development of the teeth of children, and to play an important part in the preven-of tooth decay in adults.

(b) The presence of excess fluorides, however, brings about abnormal growth of the teeth and mottling of the dental enamel.

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⇒ *Freon* (CCl_2F_2) is a colorless, odorless, noninflamable, nontoxic compound used as a refrigerant in houschold refrigerators and as a gaseous propellant in "aerosol" bombs.

- Bromine.

⇒ *Hydrogen bromide* (hydrobromic acid), Hbr, is used as a laboratory reagent in solution, and for the preparation of bromide.

(a) It is prepared by the hydrolysis of phosphorus tribromide.

$$PBr_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HBr$$

(b) It can not be prepared by the action of sulfuric acid on bromides because of oxidation-reduction complications. Phosphoric acid can be used.

$$2\ NaBr + 2\ H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + SO_2 \uparrow + 2\ H_2O + Br_2$$

$$NaBr + H_3PO_4 \xrightarrow{\Delta} NaH_2PO_4 + HBr \uparrow$$

- Iodine.

⇒ *Iodoform*, CHI_3, is prepared by the action of iodine on alcohol in alkaline solution. It is used extensively as an antiseptic.

⇒ *Hydrogen iodide* (hydroiodic acid), HI, is used to prepare iodides for photography.

(a) It is prepared by the hydrolysis of phosphorus triodide.

$$PI_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HI$$

(b) It can not be prepared by the action of sulfuric acid on iodides because of oxidation-reduction complications. Phosphoric acid can be used.

$$8\ KI + 5\ H_2SO_4 \xrightarrow{\Delta} K_2SO_4 + H_2S \uparrow + 4\ H_2O + 4\ I_2$$

$$KI + H_3PO_4 \xrightarrow{\Delta} KH_2PO_4 + HI \uparrow$$

XVI.3. Oxygen, ozone, and oxidation

XVI.3.1. Oxygen

XVI.3.1.1. Introduction

- The Chinese, as early as the eighth century, observed that air consisted of at least two different ingredients, one of which supported combustion and the other did not.

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- The ancient alchemists noted that tin, lead iron, and other metals changed to colored powders (calx) when heated (calcinated).
- The Moorish alchemist, Geber, of Sevelle (about 800) discovered that the calx weighed more than original metal and concluded that the metal combined with a part of the air.
- Leonardo da Vinci, in Italy (1452-1519) and John Mayow in England (1669) reached the same conclusion.
- However, it remained for Scheele in Sweden (1771) and Priestley in England (1774), working independently, to first prepare oxygen by heating suitable oxygen compounds, and to recognize it as a distinct substance and essential constituent of air.
- The French chemist Lavoisier, continued a series of related experiments on the rusting and calcination of metals, the burning of combustible materials, and respiration of animals.
    1. These investigations brought order out of chaos, overthrew the "phlogiston" Theory and established his name as the founder of medrn chemistry.
    2. Since the oxygen combined with sulfur, phosphorus, carbon and other non-metals to give acidic substances, Lavoisier named the new element oxygen, meaning acid former, which, to be sure, is now known to be something of a misnomer.

XVI.3.1.2. Occurrence

- Oxygen makes up approximately half by weight of the earth's crust where is occurs free or in chemical combination with all the known elements except the noble gases and fluorine.
    1. Free Oxygen. On the average, air is one-fifth oxygen by volume.
    2. Combined Oxygen.
        (a) 50.02% of the earth's crust including the ocean and atmosphere.
        (b) Eight-ninths by weight of water, H_2O.
        (c) Between 40 and 50% of all rocks, as in limestone $CaCO_3$, and sand SiO_2.
        (d) Between 50 and 70% of of plant and animal tissues.
        (e) 65% of the human body.

XVI.3.1.3. Preparation

- Laboratory Methods.
    1. By heating certain oxygen containing salts.

Potassium chlorate $\xrightarrow{\Delta}$ potassium chloride + oxygen

$2\ KClO_3 \xrightarrow{\Delta} 2\ KCl + 3\ O_2$

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Potassium nitrate $\xrightarrow{\Delta}$ potassium nitrite + oxygen

$2\ KNO_3 \xrightarrow{\Delta} 2\ KNO_2 + O_2$

2. By heating metallic oxides.

Mercuric oxide $\xrightarrow{\Delta}$ mercury + oxygen

$2\ HgO \xrightarrow{\Delta} 2\ Hg + O_2$

Barium peroxide $\xrightarrow{\Delta}$ barium oxide + oxygen

$2\ BaO_2 \xrightarrow{\Delta} 2\ BaO + O_2$

3. By the action of sodium peroxide on water.

Sodium peroxide + water $\xrightarrow{\Delta}$ sodium hydroxide + oxygen

$2\ Na_2O_2 + 2\ H_2O \xrightarrow{\Delta} 4\ NaOH + O_2$

4. By the decomposition of peroxides or hypochorites.

Hydrogen peroxide $\xrightarrow{\Delta}$ water + oxygen

$2\ H_2O_2 \xrightarrow{\Delta} 2\ H_2O + O_2$

- Commercial Methods.

1. By decomposing water with an electric curent, in the presence of dilute sulfuric acid or sodium hydroxide.

Water $\xrightarrow{\Delta}$ hydrogen + oxygen

$2\ H_2O \xrightarrow{\Delta} 2\ H_2 + O_2$

2. From liquid air.

(a) Air is a somewhat variable mixture of principally nitrogen and oxigen.

(b) When liquid air is distilled, the lower boiling nitrogen boils off first, leaving practcally pure oxygen.

XVI.3.1.4. Physical Properties

- Atomic weight, 15.9994. Atomic number, 8.
- Oxygen is a colorless, odorless, and tasteless gas.
- Critical temperature, -118°C. Critical pressure, 50 atmospheres.
- Boiling point, -183°C, as a deep blue liquid.
- Freezing point, -218.4°C, as a snow-white solid.
- Somewhat heavier than air. (1 liter weighs 1.429 g.)
- Slightly soluble in water, 4.9 cc in 100 ml of water at 0°C, and 760 mm pressure.

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XVI.3.1.5. Chemical Properties

- Valence, negative 2.
- Supports combustion and oxidation of nearly all elements, including both metals and non-metals, and many organic compounds, *e.g.*,
- 1. Metals.

$$\text{Iron} + \text{oxygen} \xrightarrow{\Delta} \text{iron oxide}$$

$$4\,Fe + 3\,O_2 \xrightarrow{\Delta} 2\,Fe_2O_3$$

- 2. Non-metals.

$$\text{Carbon} + \text{oxygen} \xrightarrow{\Delta} \text{carbon dioxide}$$

$$C + O_2 \xrightarrow{\Delta} CO_2$$

$$\text{Hydrogen} + \text{oxygen} \xrightarrow{\Delta} \text{steam}$$

$$2\,H_2 + O_2 \xrightarrow{\Delta} 2\,H_2O$$

- 3. Organic compounds.

$$\text{Sugar} + \text{oxygen} \xrightarrow{\Delta} \text{carbon dioxide} + \text{steam}$$

$$C_{12}H_{22}O_{11} + 12\,O_2 \xrightarrow{\Delta} 12\,CO_2 + 11\,H_2O$$

XVI.3.1.6. Uses

- Supports animal life.
  1. Oxygen from the air is inhaled during respiration and is absorbed through the lungs into the blood stream where it aids the oxidation of food products to furnish heat and energy to the body.
- Burning of fuels, such as coal and gasoline.
- In medical practice.
  1. Oxygen is administered for the relief of impeded respiration such as pneumonia, and cases of gaseous poisoning.
  2. Oxygen is also used with nitrous oxide and ethylene for producing anesthesia.
- Welding and cutting.
  1. Iron and steel are now commonly welded or cut by means of the oxy-acetylene or oxy-hydrogen torch.
- Carbon dust cartridges.
  1. Carbon dust, wet with liquid oxygen has been used as a substitute for dynamite in coal mining.

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- Chemical industries.
    1. Burning sulfur to make sulfur dioxide in the manufacture of sulfuric acid.
    2. Increase the oxygen content of the air blast in the Bessemer process.

XVI.3.1.7. Analytical Test

- A glowing charcoal splint, thrust into an atmosphere of oxygen that exceeds 30%, suddenly bursts into an open flame.
- Quantitatively, oxygen is usually determined by difference.

XVI.3.2. Ozone

XVI.3.2.1. Introduction

- Ozone, O_3, is an allotropic form of oxygen, distinguished by its unusual chemical activity.
- It readily tarnishes silver, has a pungent odor, and traces are frequently formed during thunder storms or around high-tension electrical apparatus.

XVI.3.2.2. Preparation

- Ozone is prepared by passing dry air between two plates charged at a potential of several thousand volts, from a source of alternating current.

XVI.3.2.3. Uses

- Sterilizing drinking water.
- Bleaching of paper pulp, fabrics and fluor.
- Resinification of oils.
- Deodorant for air in crowded interiors.

XVI.3.3. Oxidation

XVI.3.3.1. Introduction

- Stahl (1717) proposed the Phlogiston theory.
    1. All combustible material contained an invisible substance, phlogiston.
    2. When a substance burned this phlogiston escaped causting the smoke and flame.

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3. The ash was supposed to be the original substance minus its phlogiston.
4. Oils, waxes, carbon and other similar substances which left little ash or residue were supposed to be composed of nearly pure phlogiston.

- The discovery of oxygen by Scheele and Priestley and the subsequent work, particularly of Lavoisier, completely overthrew the phlogiston theory, by showing the part that oxygen plays in combustion, burning, and oxidation.
- Lavoisier's classic experiment.
    1. Mercury, when heated, combined with the oxygen in the air to form a red powder.
    2. The original mercury gained in weight, and the gain is equal to the oxygen consumed.
    3. When this red powder was again heated to a still higher temperature all the original mercury and oxygen recovered.

XVI.3.3.2. Importance of Oxidation

- Rusting of metals.
    1. Active metals are converted to oxides when exposed to air.
    2. Traces of moisture catalyze this change.
- Decay.
    1. Organic matter is slowly oxidized by the oxygen in the air, in the presence of bacteria änd moisture.
    2. Running water, containing sewage and other organic contamination, is slowly purified by oxidation and aeration.
- Spontaneous Combustion.
    1. When organic substances with a low heat condictivity are allowed to oxidize, sufficient heat may accumulate to raise then to their kindling temperature. The substance may then take fire and burn.
- Dust Explosions.
    1. Finely divided combustible material may oxidize so rapidly as to assume explosive proportions

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XVI.3.3.3. Definitions

- *Oxidation* is a chemical reaction in which oxygen combines with another element, compound or substance. We shall find later that oxidation may also involve an increase in positive valence or a decrease in negative valence.
- *Combustion* is a rapid oxidation accompanied by the libaration of noticeable heat and light.
- A *catalyst* is a substance which changes the speed of a chemical reaction without itself being permanently altered.

1. Manganese dioxide is frequently used to catalyze the decomposition of potassium chlorate.

2. A positive catalyst increases the speed of a reaction.

3. A negative catalyst decreases the speed of the reaction.

- The *heat of combustion* of an element or compound is the total quantity of heat, measured in calories, that is liberated when a gram molecule (mole) of the substance is burned.
- The *kindling temperature* is the lowest temperature at which a substance will burn.
- An *oxide* is a compound resulting from combination of oxygen with another element, either metal or non-metal.

XVI.4. Sulfur and hydrogen sulfide

XVI.4.1. Introduction

- Since sulfur occurs frequently in the free state it was known to the ancients.
- The Bible refers to it as brimstone.
- Sulfur is one of the ten or twelve elements necessary for plant and animal growth.
- It occupies a position in column six of the periodic table, just below oxygen, and hence has a similar structure to that of oxygen and many common properties.

XVI.4.2. Occurrence

- Sulfur constitutes only a mere trace of the earth's crust (0.1%) and yet in most parts of the world there are enormous deposits of both free and combined sulfur.
- Free Sulfur.

1. volcanic regions of Sicily, Italy, Japan, Mexico and South America.

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(a) The deposits of Sicily were formerly the most important source of supply.

2. The world's largest deposits of free sulfur are in Louisiana and Texas, supplying today over 80% of the world's demand.

- Combined Sulfur.
  1. Sulfides, *e.g.*, Iron pyrites, FeS_2; zinc blende, ZnS; galena, PbS; copper pyrites, $CuFeS_2$; cinnabar, HgS; stibnite, Sb_2S_3; etc.
  2. Sulfates, *e.g.*, Gypsum, $CaSO_4 \cdot 2H_2O$; barite, $BaSO_4$; Epsom salt, $MgSO_4 \cdot 7H_2O$, etc.
  3. Organic sulfur, *e.g.*, in egg yolks, seeds, hair, and brain and nervous tissue.
  4. Sulfur compounds are frequently present in petroleum and natural gas.

XVI.4.3. Allotropic Forms of Sulfur

- Sulfur is one of many different substances, both elements and compounds, that may exist in several crystalline forms (polymorphism).
  1. *Rhombic* (orthorhombic) is ordinary crystalline sulfur, readily obtained by the slow evaporation of a solution of sulfur in carbon disulfide.
  2. *Monoclinic* (prismatic) sulfur is formed by the slow cooling and crystallization of sulfur heated just above its melting point. It slowly changes to rhombic sulfur below 96°C.
  3. *Flowers of sulfur* (doubtless micro-crystalline monoclinic) is produced by suddenly cooling sulfur vapor. (B.P. 444.6°C.)
  4. *Liquid sulfur.*
     (a) Sulfur melts (about 114°C) to an amber colored limpid liquid ($S\lambda$) in which S_8 molecules predominate.
     (b) At temperature of 160°C to 180°C, it thickens and darkens forming ($S\mu$) which is but slightly soluble in carbon disulfide, and ($S\pi$) which is probably S_4.
  5. *Amorphous sulfur* can be formed by pouring boiling sulfur into cold water.
  6. *Colloidal sulfur* has been prepared by precipitation methods from solutions.
  7. The *transition temperatures* may be summarized as follows:

$$\text{Rhombic} \overset{96^\circ C}{\leftrightarrow} \text{Monoclinic} \overset{114^\circ C}{\leftrightarrow} \text{Limpid} \overset{160\text{-}180^\circ C}{\leftrightarrow} \text{Viscous} \overset{444.6^\circ C}{\leftrightarrow} \text{Vapour}$$

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XVI.4.4. Extraction of Sulfur

- Frasch Method.
    1. Certain knolls of Louisiana and Texas are underlaid with enormous deposits of sulfur, at a depth of about 500 feet.
    2. Superheated water (180°C) is forced down to the sulfur deposits through the outside pipe of a series of concentric pipes.
    3. The sulfur melts and is then forced to the top by compressed air, which is introduced through the series of concentric pipes.
    4. This produces sulfur of 99.5% purity.
- Sicilian Method.
    1. Crude sulfur, rock, and other gangue are heated by burning a portion of the sulfur present.
    2. The remaining sulfur is melted, drained off, and cast into blocks.
    3. It may be purified by distillation forming flowers of sulfur or roll sulfur.

XVI.4.5. Physical Properties

- Atomic weight, 32.064. Atomic number, 16.
- Sulfur is a pale yellow, odorless, brittle solid.
- Melting point: Rhombic, 112.8°C, Monoclinic, 119.0°C.
- Boiling point, 444.6°C.
- Specific gravity: . Rhombic, 2.07; Monoclinic, 1.957.
- Insoluble in water.Soluble in carbon disulfide, alkalies, and alcohol.

XVI.4.6. Chemical Properties

- Valence, negative 2, or positive 2, 4, and 6.
- Like oxygen, sulfur combines directly with most metals, and many non-metals, forming sulfides, but is less energetic in its action, *e.g.*,
    1. Metals.

$$Zn + S \rightarrow ZnS$$

$$2\ Ag + S \rightarrow Ag_2S$$ (responsible for tarnishing of silver).

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$$Fe + S \rightarrow FeS$$

2. Non-metals.

$$H_2 + S \xrightarrow{\Delta} H_2S$$

$$2\,S + Cl_2 \xrightarrow{\Delta} S_2Cl_2$$

$$C + 2\,S \xrightarrow{\Delta} CS_2$$

$$S + O_2 \xrightarrow{\Delta} SO_2,\ 2\,SO_2 + O_2 \xrightarrow{\text{catalyst}} 2\,SO_3$$

XVI.4.7. Uses

- *Sulfuric acid.* Large quantities of sulfur are burned to produce sulfur dioxide, SO_2, in the manufacture of sulfuric acid.
- *Sulfur compounds.* Sulfur is combined with carbon in an electric furnace to produce carbon disulfide. A sulfide of phosphorus, P_4S_3, is used extensively in the match industry.
- *Black gunpowder.* Black gun powder consists of a mixture of sulfur, charcoal, and potassium nitrate, KNO_3.
- *Agriculture.* Sulfur is used alone or is mixed with lime as lime-sulfur to destroy fungi in orchards and vineyards. Mixed with ground phosphate it is sometimes applied to the soil as a fertilizer. Sulfur has been applied to selenium soils to counteract the absorption of toxic selenium by many growing plants.
- *Acid-proof cements.* Molten sulfur and sand can be poured like concrete. The resulting cement is acid proof, has fair mechanical strength, and is an excellent heat and electrical insulator.
- *Constructions materials.* Wood, paper, cardboard, and fabrics are sometimes impregnated with molten sulfur to make them more resistant to moisture, insects, and fungi.
- *Vulcanizing rubber.* Sulfur and sulfur monochloride, S_2Cl_2, are used extensively in vulcanizing rubber.
- *Sulfites, sulfates, and thiosulfates.* Many sulfites, sulfates and thiosulfates are prepared by the direct or indirect use of sulfur.
- *Steel.* Sulfur is sometimes added to steel to be used in the manufacture of steel screws.
- *Mineral oils.* Sulfur is frequently dissolved in vegetable oils, and then incorporated in mineral oils for use as a lubricant for steel-cutting tools.
- *Parasiticide.* Sulfur candles burn readily in air to form sulfur dioxide, SO_2, which is used in fumigation.

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XVI.4.8. Analytical Test

- The free element may be recognized by the pungent odor of sulfur dioxide when sulfur is burned, or by dissolving it in hot alkali solution and placing a drop of the solution on a piece of metallic silver. A dark stain Ag_2S develops.
- Quantitatively sulfur is usually determined by oxidation to the sulfate. The sulfate is then precipitated and weighed as barium sulfate, $BaSO_4$.

$$2\ S + 3\ O_2 + 2\ H_2O \rightarrow 2\ H_2SO_4$$

$$H_2SO_4 + BaCl_2 \rightarrow 2\ HCl + BaSO_4 \downarrow$$

XVI.4.9. Hydrogen sulfide

XVI.4.9.1. Introduction

- Hydrogen sulfide is a colorless, poisonous gas with an offensive odor resembling that of spoiled eggs.
- It occurs wherever plant and animal matter decays with a limited supply of air.
- Many mineral springs owe their odor and taste to its presence.
- It is found in natural gas, coal gas, and cracked hydrocarbons.

XVI.4.9.2. Preparation

- Action of dilute, non-oxidizing acid on a sulfide.

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S \uparrow$$

$$Na_2S + 2\ HCl \rightarrow 2\ NaCl + H_2S \uparrow$$

- Direct union of hydrogen and sulfur.

$$H_2 + S \xrightarrow{\Delta} H_2S \uparrow$$

- Heating paraffin and sulfur.

XVI.4.9.3. Physical Properties

- A colorless, poisonous gas with an offensive odor.
- Slightly heavier than air.
- Melting point, -83°C. Boiling point, -60°C.
- Solubility in water, 290 cc in 100 ml at 20°C.

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- Extremely poisonous when inhaled. Small amounts produce severe headaches, larger amounts produce death.
- The water solution behaves as a typical weak, dibasic acid (Hydrosulfuric acid).

XVI.4.9.4. Chemical Properties

- It acts as a slightly active acid, forming acid and normal salts.

$$H_2S + NaOH \rightarrow NaHS + H_2O$$

$$NaHS + NaOH \rightarrow Na_2S + H_2O$$

- It reacts with many metallic salts forming characteristically colored sulfide precipitates.

$$Pb(NO_3)_2 + H_2S \rightarrow 2\ HNO_3 + PbS \downarrow \quad \text{(black)}$$

$$SnCl_2 + H_2S \rightarrow 2\ HCl + SnS \downarrow \quad \text{(braun)}$$

$$2\ SbCl_3 + 3\ H_2S \rightarrow 6\ HCl + Sb_2S_3 \downarrow \quad \text{(orange)}$$

$$Cd(NO_3)_2 + H_2S \rightarrow 2\ HNO_3 + CdS \downarrow \quad \text{(yellow)}$$

$$Zn(NO_3)_2 + H_2S \rightarrow 2\ HNO_3 + ZnS \downarrow \quad \text{(white)}$$

1. Hydrogen sulfide is an important analytical reagent, producing many insoluble sulfides.

   (a) One group is insoluble in dilute acid, the other group is soluble in dilute acids but insoluble in basic solutions.

   (b) Advantage is taken of these facts in making numerous separations.

- It acts as a reducing agent.

$$SO_2 + 2\ H_2S \rightarrow 2\ H_2O + 3\ S$$

$$2\ HNO_3 + 3\ H_2S \rightarrow 2\ NO + 4\ H_2O + 3\ S$$

- Hydrogen sulfide burns in air.

$$2\ H_2S + 3\ O_2 \rightarrow 2\ H_2O + 2\ SO_2$$

- Hydrogen sulfide reacts with numerous metals.

$$2\ Ag + H_2S \rightarrow Ag_2S + H_2$$

$$Cu + H_2S \rightarrow CuS + H_2$$

XVI.4.9.5. Uses

- Hydrogen sulfide is an important analytical reagent, used either as a gas or in solution.
- An important laboratory reducing agent.
- Preparation of metallic sulfides, many of which are used for painting pigments.

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XVI.4.9.6. Analytical Test

- Hydrogen sulfide may be recognized by its odor, or ability to darken lead acetate paper. Sulfides libarate hydrogen sulfide when treated with dilute acids.

$$FeS + 2\ HCl \rightarrow FeCl_2 + H_2S\ \uparrow$$

$$H_2S + Pb(C_2H_3O_2)_2 \rightarrow 2\ HC_2H_3O_2 + PbS\ \text{(black)}$$

XVI.5. The oxides and oxygen acids of sulfur

XVI.5.1. Introduction

- The great German chemist, Justus von Liebig once stated that the civilization of any country is directly proportional to the amount of sulfuric acid used.
  1. It is interesting to note in this connection that the United States today is the largest per capita consumer of sulfuric acid of any nation.
- Sulfur is one of the cheapest and most useful of all raw materials, the very cornerstone of the great chemical industries.
  1. There is scarcely a single manufactured article today from Portland cement to finger nail polish that has not met sulfur, directly or indirectly, in its preparation.
  2. The oxides and acids of sulfur are among its most important compounds.

XVI.5.2. Preparation

- Sulfur Dioxide.
  1. By burning sulfur in air. (Commercial.)

$$S + O_2 \rightarrow SO_2$$

  2. By burning metallic sulfides. (Commercial.)

$$4\ FeS_2 + 11\ O_2 \xrightarrow{\Delta} 2\ Fe_2O_3 + 8\ SO_2\ \uparrow$$

$$2\ PbS + 3\ O_2 \xrightarrow{\Delta} 2\ PbO + 2\ SO_2\ \uparrow$$

$$2\ ZnS + 3\ O_2 \xrightarrow{\Delta} 2\ ZnO + 2\ SO_2\ \uparrow$$

  3. By treating sulfites with non-volatile acids.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\ \uparrow$$

  4. By the reaction of sulfuric acid with metals, non-metals, and other reducing agents.

$$2\ H_2SO_4 + Cu \rightarrow CuSO_4 + 2\ H_2O + SO_2\ \uparrow$$

$$2\ H_2SO_4 + S \rightarrow 2\ H_2O + 3\ SO_2\ \uparrow$$

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$$2\ H_2SO_4 + 2\ NaBr \rightarrow Na_2SO_4 + 2\ H_2O + Br_2 + SO_2\ \uparrow$$

- Sulfurous Acid.

  1. By dissolving sulfur dioxide in water.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

XVI.5.3. Physical Properties

- Sulfur Dioxide.

  1. Sulfur dioxide is a colorless gas with a pungent odor of burning sulfur.
  2. Sulfur dioxide is 2.2 times as heavy as air.
  3. Readily liquefied at 25°C, by 4 atmospheres pressure, or at -10°C, by 1 atmosphere.
  4. Heat of vaporization, 91.3 calories per gram. Therefore, used in household refrigerators.

- Excellent solvent for waxes, resins, and cellulose acetate.
- Dissolves and reacts with water to the extent of 50 parts to 1 at 20°C, and 80 parts to 1 at 0°C, forming sulfurous acid. $SO_2 + H_2O \rightarrow H_2SO_3$.

XVI.5.4. Chemical Properties

- Sulfur Dioxide.

  1. Most properties of sulfur dioxide depend upon traces of moisture which forms sulfurous acid.
  2. It dissolves in and reacts with water.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

  3. It reacts with oxygen in the presence of suitable catalysts to form sulfur trioxide.

$$2\ SO_2 + O_2 \xrightarrow{\text{catalyst}} 2\ SO_3$$

- Sulfurous Acid.

  1. Sulfurous acid is only moderately active, forming acid and normal sulfites.

$$H_2SO_3 + NaOH \rightarrow NaHSO_3 + H_2O$$

$$NaHSO_3 + NaOH \rightarrow Na_2SO_3 + H_2O$$

  2. Sulfurous acid and sulfites are important reducing agents.

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O \rightarrow 2\ FeSO_4 + 2\ H_2SO_4$$

$$Br_2 + H_2SO_3 + H_2O \rightarrow 2\ HBr + H_2SO_4$$

$$2\ KMnO_4 + 5\ H_2SO_3 \rightarrow K_2SO_4 + 2\ MnSO_4 + 2\ H_2SO_4 + 3\ H_2O$$

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$$K_2Cr_2O_7 + 3\ H_2SO_3 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\ H_2O$$

$$2\ HNO_3 + 3\ H_2SO_3 \rightarrow H_2O + 2\ NO + 3\ H_2SO_4$$

3. Sulfurous acid and sulfites are slowly oxidized by air.

$$2\ Na_2SO_3 + O_2 \rightarrow 2\ Na_2SO_4$$

4. Sulfurous acid is relatively unstable to heat and has never been isolated.

$$H_2SO_3 \rightarrow H_2O + SO_2\ \uparrow$$

XVI.5.5. Uses

- Manufacture of sulfuric acid.
  1. This is by far the most important use.
- Bleaching.
  1. Bleaching is probably due to the formation of colorless addition compounds.
     (a) Since these compounds are often unstable, the bleaching by sulfur dioxide is not very permanent.
  2. It is used with silks, wool, hair, straw, sponges and other products that would be destroyed by chlorine.
- Disinfectant.
  1. Its effect is probably due to its activity and ability to exclude oxygen.
- Household fumigation.
  1. It is been largely displaced with formaldehyde.
- Preparation of corn starch.

1. The corn is soaked for several days in dilute sulfurous acid, which prevents fermentation.

- Paper for sulfite process.
  1. Calcium acid sulfite, $CaH_2(SO_3)_2$, is used extensively in the paper industry.
  2. It is prepared by passing an excess of sulfur dioxide into a suspention of slaked lime, $Ca(OH)_2$.
- Bleach and food preservative.
  1. This use is questionable and particularly it used in excess.
- Household refrigeration.
  1. Some refrigerators make use of the high heat of vaporization of sulfur dioxide.
- Organic solvent.

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1. Liquid sulfur dioxide is used as a solvent for waxes, resins, and cellulose acetate in the preparation of films, plastics, and rayon of this type.

- Lubricating oils.

1. Liquid sulfur dioxide is used as a selective solvent for the improvement of lubricating oil.

XVI.5.6. Sulfur trioxide and sulfuric acid

XVI.5.6.1. Introduction

- Sulfur trioxide.

1. Sulfur trioxide is prepared by the oxidation of sulfur dioxide in the presence of suitable catalysts.

(a) Platinum, iron oxide, vanadium pentoxide, V_2O_5, nitric acid, and the oxides of nitrogen have been variously used.

$$2\ SO_2 + O_2 \xrightarrow{\text{catalyst}} 2\ SO_3$$

- Contact sulfuric acid.

1. Sulfur or pyrite is burned in air to form sulfur dioxide.
2. The sulfur dioxide is carfully purified and dried.
3. The purified sulfur dioxide is mixed with air, passed over a heated catalyst, and converted to sulfur trioxide.
4. The sulfur trioxide is dissolved with a spray of concentrated sulfuric acid forming pyrosulfuric acid, $H_2S_2O_7$.
5. The pyrosulfuric acid is diluted with a quantity of water equivalent to the excess sulfur trioxide.
6. Equations:

$$S + O_2 \rightarrow SO_2$$

$$2\ SO_2 + O_2 \xrightarrow{\text{catalyst}} 2\ SO_3$$

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \rightarrow 2\ H_2SO_4$$

- Lead chamber sulfuric acid.

1, Pyrite or sulfur is burned in air to produce sulfur dioxide.
2. The resulting sulfur dioxide is purified to remove traces of arsenic and dust.

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3. The purified gases, while still hot, are passed up through the Glover tower where nitrogen dioxide, NO_2, is added. Some acid is produced at this point.
4. The unreacted sulfur dioxide is passed through a series of lead-lined chambers where additional air and steam are added. Here additional sulfuric acid is produced.
5. The oxides of nitrogen, escaping from the last of the chambers, are recovered by dissolving them in concentrated sulfuric acid in the Gay-Lussac tower forming nitrosyl sulfuric acid. The solution of nitrosyl sulfuric acid is pumped to the top of the Glover tower.
6. Equations:

(a) Glowr tower.

$$2\ SO_2(OH)(ONO) + H_2O \rightarrow 2\ H_2SO_4 + NO + NO_2$$

(b) Lead-lined chambers.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$$

(c) Gay-Lussac tower.

$$NO + NO_2 + 2\ H_2SO_4 \rightarrow 2\ SO_2(OH)(ONO) + H_2O$$

XVI.5.6.2. Physical Properties

- Sulfur trioxide.

1. A colorless liquid, freezing at 16.8°C.
2. Solid sulfur trioxide is polymorphic, the three forms melting at 16.8°, 32.5°, and 62.2°C.
3. It is more readily soluble in sulfuric acid than water.

- Sulfuric acid.

1. A colorless, oily liquid.
2. Density of 96% acid, 1.835.
3. Freezing point, 10.49°C.
4. Boiling point, 338°C, at which temperature it decomposes somewhat, and forms a constant-boiling mixture with water containing 1.67% water.

XVI.5.6.3. Chemical Properties

- Sulfur trioxide.

1. Dissolves in and reacts with water.

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$$SO_2 + H_2O \rightarrow H_2SO_4$$

2. Reacts with sulfuric acid forming pyrosulfuric acid.

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

3. It is vigorous oxidizing agent, *e.g.*,

$$Zn + SO_3 + H_2O \rightarrow ZnSO_4 + H_2$$

- Sulfuric acid.

1. Dilute sulfuric acid behaves as a typical acid reacting with active metals, most metallic oxides, sulfites, sulfides, carbonates, and hydroxides to form acid and natural sulfates.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 4\,H_2O + SO_2 \uparrow$$

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S \uparrow$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$$

$$NaOH + NaHSO_4 \rightarrow Na_2SO_4 + H_2O$$

2. Concentrated sulfuric acid (90 to 96%) acts as a strong oxidizing agent.

$$Cu + 2\,H_2SO_4 \rightarrow CuSO_4 + 2\,H_2O + SO_2 \uparrow$$

$$8\,KI + 5\,H_2SO_4 \rightarrow 4\,K_2SO_4 + 4\,H_2O + 4\,I_2 + H_2S \uparrow$$

3. Concentrated sulfuric acid acts as a powerful dehydrating agent, and is frequently used to dry gases. It also extracts water from many organic compounds.

$$C_{12}H_{22}O_{11}\ \text{(sugar)} \xrightarrow{\text{con. } H_2SO_4} 12\,C + 11\,H_2O$$

4. It displaces other volatile acids from their salts.

$$H_2SO_4 + NaNO_3 \xrightarrow{\Delta} NaHSO_4 + HNO_3 \uparrow$$

$$H_2SO_4 + NaCl \xrightarrow{\Delta} NaHSO_4 + HCl \uparrow$$

5. It reacts with water liberating much heat with the formation of hydrates such as $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, $H_2SO_4 \cdot 4H_2O$, etc.

XVI.5.6.4. Uses

- Fertilizer industry.

1. Rock phosphate is rendered soluble by treatement with dilute sulfuric acid.
2. Ammonia is reacted with sulfuric acid to produce ammonium sulfate.

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- Refining petroleum.

1. Objectionable sulfur and tarry compounds are remove by agitation with sulfuric acid.

- Chemical industry.

1. Products prepared by the use of sulfuric acid include other acids, ether, and metallic sulfates.

- Dyes and medicinals.

1. Used for sulfonation and dehydration purposes in connection with coal tar products.

- Pickling steel.

1. For cleaning metals and their oxides before galvanizing, electroplating, soldering, or enameling.

- Metallurgy.

1. Copper is eventually recovered from its ore by use of sulfuric acid.

- Manufacture and explosives.

1 Mixture of sulfuric and nitric acid are used in the manufacture of most explosives such as dynamite, smokelesspowder, T.N.T., and picric acid.

- Nitrocellulose products, etc.

1. Photographic films; rayon; cotton, wool, and linen fabrics; rubber; lacquers and many related products are made by the direct use of sulfuric acid.

- Storage batteries.

1. Sulfuric acid is used as the electrilyte in lead storage batteries.

- Electroplating.

1. Most electroplating baths contain sulfuric acid.

XVI.5.6.5. Analytical Test

- Sulphates are readily precipitated by the use of a solution of barium chloride.

1. The preipitate is insoluble in dilute hydrochloric acid.
2. This is the basis for both the qualitative and quantitative estimation of sulfates.

$$H_2SO_4 + BaCl_2 \rightarrow 2\ HCl + BaSO_4 \downarrow$$

- Sulfites liberate sulfur dioxide, a gas with a characteristic odor which bleaches potassium permanganate solution, when treated with acids.

$$Na_2SO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2O + SO_2 \uparrow$$

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XVI.6. Nitrogen and the atmosphere

XVI.6.1. Introduction

- Nitrogen, a relatively inert gas, is the first member of group five of the periodic table.
  1. It was discovered by Daniel Rutherford in 1772.
  2. It is an extremely important element in plant and animal growth.
  3. Recent developments of industrial methods for its fixation from the air are among the most important scientific discoveries of man.

XVI.6.2. Occurrence

- Free nitrogen.

1. Air is about three-fourths elementary nitrogen, N_2, by weight, or four-fifths by volume.

- Combined nitrogen.
  1. Great amounts of sodium nitrate (Chile salpeter) in Chile and South Africa.
  2. Traces of ammonium salts in drier parts of the world.
  3. Nitrogen is found in all plant and animal matter as proteins.
  4. All fertile soils contain nitrogen as ammonium salts, nitrites, and nitrates.

XVI.6.3. Preparation

- Laboratory Methods.
  1. By removing the oxygen from air with burning phosphorus in the presence of water.
     (a) The phosphorus pentoxide formed dissolves in the water leaving nitrogen with traces of impurities originally present in the air.

$$4\ P + 5\ O_2 \rightarrow 2\ P_2O_5$$

$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4$$

  2. By heating a solution of ammonium chloride and sodium nitrite.

$$NH_4Cl + NaNO_2 \xrightarrow{\Delta} NH_4NO_2 + NaCl$$

$$NH_4NO_2 \xrightarrow{\Delta} 2\ H_2O + N_2$$

  3. By bubbling air through a solution of ammonium chloride and ammonium hydroxide in the presence of copper turnings. The copper is oxidized leaving the nitrogen.

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4. By passing ammonia over heated copper oxide.

$$Na_2SO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2O + SO_2 \uparrow$$

- Miscellaneous methods.

$$MnO_2 + 4\ NH_4NO_3 \rightarrow Mn(NO_3)_2 + 8\ H_2O + 3\ N_2 \uparrow$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + 4\ H_2O + N_2 \uparrow$$

$$2\ P + 5\ NH_4NO_3 \rightarrow 2\ H_3PO_4 + 7\ H_2O + N_2 \uparrow$$

$$CO(NH_2)_2\ (\text{urea}) + 2\ HNO_2 \rightarrow CO_2 + 3\ H_2O + 2\ N_2 \uparrow$$

- Commercial Methods.

1. By the fractional distillation of liquid air.

(a) Nitrogen boils off first (B.P. -195.8°C) leaving oxygen (B.P. -183°C).

XVI.6.4. Physical Properties

- Atomic weight, 14.007. Atomic number, 7.
- Nitrogen is a colorless, odorless and tasteless gas.
- Boiling point, -195.8°C, as a colorless liquid.
- Freezing point, -209.9°C.
- Somewhat lighter than air (1 liter weighs 1.2506 g).
- Only slightly soluble in water, 0.00189 g in 100 g of water at 20°C, and 1 atmosphere pressure.

XVI.6.5. Chemical Properties

- Known valences, negative 3, and positive 1, 2, 3, 4, and 5.
- Nitrogen is characterized by its outstanding inactivity, but reacts with hydrogen, oxygen, active metals, and a few other compounds under compulsion.

1. It reacts with hydrogen under pressure in the presence of catalysts.

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

2. It reacts with oxygen in an electric arc.

$$N_2 + O_2 \xrightarrow{\Delta} 2\ NO$$

3. It reacts with heated, active metals, *e.g.*,

$$N_2 + 3\ Mg \xrightarrow{\Delta} Mg_3N_2$$

4. It reacts with calcium carbide to form calcium cyannamide.

$$N_2 + CaC_2 \rightarrow CaCN_2 + C$$

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5. It reacts to form cyanides. (Bucher process.)

$$N_2 + 4C + Na_2CO_3 \rightarrow 2\ NaCN + 3\ CO$$

XVI.6.6. Uses

- Ammonia and Cyanamide.
    1. These are important fertilizer materials and are made directly from nitrogen in the air. Annual demands often exceed a milion tons.
- Inert gas.
    1. Because of its inert nature, nitrogen is often used in the laboratory to dilute more active gases, and exclude oxygen from apparatus.
- Plant food.
    1. Nitrogen compounds are essential for plant and animal life and growth.
- Nitric acid.
    1. Nitric acid is produced industrially today from nitrogen in the air.
- Thermometrs.
    1. The best high temperature thermometers are usually filled with nitrogen to prevent the evaporation of the mercury.

XVI.6.7. Analytical Test

- Duma's Method.
    1. The weighed sample is ignited with copper oxide in an atmosphere of carbon dioxide.
    2. The free nitrogen liberated is collected over potassium hydroxide solution, measured, and its weight calculated.
- Kjeldahl Method.
    1. The weighed sample is digested with concentrated sulfuric acid in the presence of potassium sulfate and copper sulfate.
    2. An excess of sodium hydroxide solution is then added and the ammonia that is liberated is distilled into standard acid.
    3. By titration, the amount of ammonia and nitrogen orginally present is calculated.

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THE ATMOSPHERE

XVI.6.8.1. Introduction

- The ancients considere air to be one of the four elements, air, earth, fire, and water.
- We now know it to be a mixture of many gases, completely surrounding the earth to a depth of many miles, exerting an average pressure of 14.7 pounds per square inch.

XVI.6.8.2. Composition

	Per Cent by Volume	*Per Cent by Weight*
Nitrogen	78.0	75.58
Oxygen	21.0	23.08
Argon	.9	1.28
Carbon dioxide	.03	.53
Hydrogen	.01	.001
Neon	.0015	
Helium	.00015	
Other gases	.05835	.006
Total	100.00	100.00

XVI.6.8.3. Air as a Mixture

- The composition of the atmosphere varies from place to place, time to time, and at different altitudes.
- Air can be readily separated into its components by fractional distillation.
- Air placed in contact with a typical solvent, such as water, is altered in composition due to the different solubilities of the components present.
- The physical properties of air are the average of its component gases.
- No chemical formula can written for air that will coincide with its percentage composition.
- No energy is absorbed or liberated when the component gases are intermingled to produce air.

XVI.6.8.4. Function of the Component Gases

- Oxygen.
  1. Supports animal life and combustion. Aids in decay, fermentation, and oxidation.
- Nitrogen.
  1. Essential for plant growth, and indirectly for animal life.
  2. Serves as a diluant for the oxygen in the atmosphere.

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- Carbon dioxide.
    1. An essential plant food where it combines with water to produce carbonhydrates in the presence of chlorophyll under the influence of sunlight.
- Water vapor.
    1. It prevents excessive evaporation from plants and animals and supplies moisture for growth.
    2. The quantity of moisture in air is expressed as the humidity.
        (a) Absolute humidity is the amount of water vapor per unit volume of gas.
        (b) Relative humidity is the ratio of the actual amount of water vapor present to the maximum amount possible at that temperature.
- Dust particles.
    1. Furnish nuclei around which moisture condenses during precipitation.
    2. Produce colored sunsets.
- Other gases.
    1. The rare gases, hydrogen, hydrogen sulfide, sulfur dioxide, ammonia, ozone, hydrogen peroxide, and oxides of nitrogen are present in traces only.

XVI.6.8.5. THE RARE (or Noble) GASES

XVI.6.8.5.1. Introduction

- The memebers of the zero group of the periodic table, helium, neon, argon, krypton, xenon, and radon, are known as the rare gases.

1. Since their valence shell is completely filled, they show no ordinary chemical activity.

XVI.6.8.5.2. Discovery

- Helium.
    1. By Sir Norman Lockyer, 1668, in the spectrum of the sun.
    2. Isolated by Ramsay in 1895 from uraninite.
    3. Name means the *sun*, Greek "helios."
- Neon.
    1. By Ramsay and Travers in 1898 in air.
    2. Name means *new*, Greek "neos."

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- Argon.
    1. Presence in air suspected by Cavendish in 1785.
    2. Discovered by Rayleigh and Ramsay in air in 1894.
    3. Name means *inactive*, Greek "argon."
- Krypton.
    1. By Ramsay and Travers in residues of liquid air in 1898.
    2. Name means *hidden*, Greek "kryptos."
- Xenon.
    1. By Ramsay and Travers in residues of liquid air in 1898.
    2. Name means *stranger*, Greek "xenon."
- Radon.
    1. By Dorn in 1900 and called radium emanation.
    2. Isolated in 1908 by Ramsay and Gray who called it niton, Latin, "nitens" meaning *shining*.

XVI.6.8.5.3. Preparation

- Helium.
    1. From natural gas wells of Kansas and Texas, which contain up to 2% of helium.
- Neon and Argon.
    1. By the distillation of residues from liquid air.

XVI.6.8.5.4. Physical Properties

- Helium.
    1. Atomic weight, 4.003. Atomic number, 2.
    2. Second lightest gas known. (1 liter weighs 0.177 g.)
    3. Boiling point, -269.9°C. Freezing point, -272.2°C.
    4. Last gas to be liquefied.
    5. Has one atom per molecule, He.
    6. Slightly soluble in water.
- Neon.
    1. Atomic weight, 20.183. Atomic number, 10.
    2. Boiling point, -245.9°C. Freezing point, -248.67°C.

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3. Has one atom per molecule, Ne.

4. One liter weighs 0.9002 g.

6. Slightly soluble in water.

- Argon.

1. Atomic weight, 39.948. Atomic number, 18.

2. Boiling point, -185.7°C. Freezing point, -189.2°C.

3. One liter weighs 1.782 g.

4. Relatively soluble in water.

5. Absorbed by charcoal.

XVI.6.8.5.5. Uses

- Helium.

1. Filling balloons and caissons.

- Neon.

1. To produce the red glow in electric signs.

- Argon.

1. Filling electric light bulbs and electric signs.

XVI.7 Ammonia and ammonium salts

XVI.7.1. Introduction

- Ammonia was originally made by the destructive distillation of hoofs, horns, and other nitrogenous materials, and the solution of the gas was called, "spirits of hartshorn."
- Priestley, in 1774 collected samples of the gas over mercury and studied its properties.
- Berthollet, in 1785 proved that ammonia was a compound of nitrogen and hydrogen.

XVI.7.2. Preparation

- Laboratory Methods.

1. Decomposition of ammonium hydroxide with heat.

$$NH_4OH \xrightarrow{\Delta} H_2O + NH_3$$

2. Reaction of an ammonium salt and a strong base.

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$$(NH_4)_2SO_4 + Ca(OH)_2 \xrightarrow{\Delta} CaSO_4 + 2\,H_2O + 2\,NH_3\uparrow$$

$$NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + H_2O + NH_3\uparrow$$

3. By the action of moisture on a metallic amide or nitride.

$$NaNH_2 + H_2O \rightarrow NaOH + NH_3\uparrow$$

$$Mg_3N_2 + 6\,H_2O \rightarrow 3\,Mg(OH)_2 + 2\,NH_3\uparrow$$

$$AlN + 3\,H_2O \rightarrow Al(OH)_3 + NH_3\uparrow$$

- Commercial Methods.

1. Direct reaction of nitrogen and hydrogen at elevated pressures and temperatures in the presence of catalysts. (Haber process.)

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

2. From calcium cyanamide and superheated steam.

$$CaCN_2 + 3\,H_2O \xrightarrow{\Delta} CaCO_3 + 2\,NH_3\uparrow$$

3. By-product ammonia from coal and shale.

XVI.7.3. Physical Properties

- Ammonia is a colorless gas with a pungent odor.
- It is lighter than air and is colected by upward displacement.
- Boiling point, -33.4°C. Melting point, -78°C.
- Critical temperature, 133°C. Critical pressure, 112 atmospheres. Therefore, easily liquefied.
- Heat of vaporization, 330 calories per gram. Hence, used extensively in refrigeration.
- As a solvent liquid ammonia resembles water more closely than any other substance.
- Extremely soluble in water. One volume of water dissolves 1300 volumes of ammonia.

XVI.7.4. Chemical Properties

- Dissolves in and reacts with water forming ammonium hydroxide.

$$NH_3 + H_2O \rightarrow NH_4OH$$

- Ammonia reacts directly with acids to form ammonium salts.

$$NH_3 + HCl \rightarrow NH_4Cl$$

$$2\,NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

- Ammonia burns in pure oxygen.

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$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$$

- Ammonia, in the presence of platinum, is oxidized to nitric oxide.

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

- Reacts with many metallic salts forming soluble complexes.

$$CuSO_4 + 4\ NH_3 \rightarrow Cu(NH_3)_4SO_4$$

$$AgCl + 2\ NH_3 \rightarrow Ag(NH_3)_2Cl$$

$$CoCl_3 + 6\ NH_3 \rightarrow Co(NH_3)_6Cl_3$$

- Ammonia is decomposed by heat.

$$2\ NH_3 \xrightarrow{\Delta} N_2 + 3\ H_2$$

- Ammonia reacts with active metals to form amides, imides, and nitrides.

$$2\ Na + 2\ NH_3 \rightarrow H_2 + 2\ NaNH_2 \text{ (sodium amide).}$$

$$2\ Ag + NH_3 \rightarrow H_2 + Ag_2NH \text{ (siver imide).}$$

$$6\ Li + 2\ NH_3 \rightarrow 3\ H_2 + 2\ Li_3N \text{ (lithium nitride).}$$

XVI.7.5. Uses

- Nitric acid.
  1. Ammonia, in the presence of platinum, is oxidized to nitric oxide, which in turn is converted into nitric acid.
- Preparation of Baking and Washing Soda.
  1. Ammonia is used in the Solvay process for manufacturing baking and washing soda.
- Ammonium Salts.
  1. Huge quantities of ammonia are converted into and marketed as ammonium salts, which have important uses of their own.
- Refrigeration.
  1. Liquid ammonia is used as a refrigerant and in the manufacture of ice.

XVI.7.6. Heavy Ammonia

- Magnesium nitride reacts with "heavy water" to produce "heavy ammonia."

$$Mg_3N_2 + 6\ D_2O \rightarrow 3\ Mg(OD)_2 + 2\ ND_3\ \uparrow$$

1. It is a gas with the same odor as ordinary ammonia but with a density 1.174 times greater.

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2. Other physical properties differ from regular ammonia.
3. Since there are three known isotopes of hydrogen and two of nitrogen, there are 20 possible varieties of ammonia.

XVI.7.7. Analytical Test

- Ammonium salts are characterized by their ability to liberate ammonia gas when treated with a strong base.
    1. The ammonia may be recognized by its characteristic odor or ability to turn moist red litmus paper blue.
- Ammonia and ammonium salts in water may be detected by the use of *Nessler's reagent.*
    1. A yellow to orange-yellow coloration, $NH_2Hg_2I_3$, is produced.
    2. The test is sensitive to one part in ten million.

XVI.7.8. Ammonium Compounds

⇒ Ammonium Hydroxide, NH_4OH.
    1. It is an important cleaning fluid (household ammonia), a weak base, and is used to make ammonium salts and other insoluble hydroxides.

⇒ Ammonium Sulfate, $(NH_4)_2SO_4$.
    1. It is prepared by dissolving ammonia in sulfuric acid.
    2. It is used principally as a fertilizer.

⇒ Ammonium Chloride, NH_4Cl.
    1. It is used in dry cells, and for cleaning metallic surfaces for soldering.

⇒ Ammonium Nitrate, NH_4NO_3.
    1. It is added to numerous commercial explosives.
    2. It is used as a laboratory source of nitrous oxide (laughing gas), N_2O.

⇒ Ammonium Bicarbonate, NH_4HCO_3.
    1. It is used in backing crackers.
    2. It is an intermediate product in the Solvay process for making baking and washing soda.

⇒ Calcium Ammonium Phosphate, $Ca(NH_4)_4(PO_4)_2$.
    1. It is now an important fertilizer.

⇒ Ammonium Sulfide, $(NH_4)_2S$.
    1. It is an important analytical reagent.
    2.

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XVI.8 Oxides of nitrogen and nitric acid

XVI.8.1. Introduction

- Nitrogen forms at least five known oxides with oxygen.
  1. Nitrogen pentoxide, N_2O_5.
  2. Nitrogen tetroxide $\leftrightarrow$ nitrogen dioxide, $N_2O_4 \leftrightarrow 2\ NO_2$.
  3. Nitrogen trioxide, N_2O_3.
  4. Nitric oxide, NO.
  5. Nitrous oxide, N_2O.
  6. The valences of the nitrogen are positive 5, 4, 3, 2, and 1 respectively.
- This series of oxides furnishes another striking example of the law of multiple proportions.
- These oxides are closely related to the two common acids, HNO_3, nitric acid; and HNO_2, nitrous acid.

XVI.8.2. Preparation

- Nitrous oxide, N_2O.
  1. By heating ammonium nitrate.

$$NH_4NO_3 \xrightarrow{\Delta} 2\ H_2O + N_2O$$

- Nitric oxide, NO.
  1. By the interaction of metallic copper and dilute nitric acid. (Laboratory method.)

$$Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO\uparrow$$

  2. Dilute sulfuric acid reacts with dilute nitric acid in the presence of ferrous sulfate. (Laboratory method.)

$$3\ H_2SO_4 + 2\ HNO_3 + 6\ FeSO_4 \rightarrow 3\ Fe_2(SO_4)_3 + 4\ H_2O + 2\ NO\uparrow$$

  3. By passing air through an electric arc. (Commercial method.)

$$N_2 + O_2 \rightarrow 2\ NO$$

  4. Ammonia is oxidized in the presence of a catalyst. (Commercial method.)

$$4\ NH_3 + 5\ O_2 \rightarrow 6\ H_2O + 4\ NO$$

- Nitogen trioxide, N_2O_3.
  1. Nitrogen trioxide is the anhydride of nitrous acid.

$$N_2O_3 + H_2O \rightarrow 2\ HNO_2$$

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2. The acid is very unstable and readily evolves a mixture of nitric oxide and nitrogen dioxide, since the trioxide is itself unstable at ordinary temperatures.

$$2\ HNO_2 \rightarrow H_2O + N_2O_3 \rightarrow H_2O + NO + NO_2$$

- Nitrogen dioxide, NO_2.

1. By the action of oxygen on nitric oxide.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

2. By heating the nitrates of heavy metals, *e.g.*,

$$2\ Pb(NO_3)_2 \xrightarrow{\Delta} 2\ PbO + O_2 + 4\ NO_2$$

3. By adding formaldehyde solution to concentrated nitric acid.

$$HCHO + 4\ HNO_3 \rightarrow 3\ H_2O + CO_2 \uparrow + 4\ NO_2 \uparrow$$

- Nitrogen pentoxide, N_2O_5.

1. By the action of phosphorus pentoxide on nitric acid.

$$P_2O_5 + 2\ HNO_3 \rightarrow 2\ HPO_3 + N_2O_5$$

XVI.8.3. Physical Properties

- Nitrous oxide, N_2O.

1. A colorless gas, easily liquefied at 20°C, but a pressure of 50 atmospheres.
2. Faint odor and sweet taste.
3. Soluble to the extent of 1.3 cc in 1 ml of water at 20°C.

- Nitric oxide, NO.

1. A colorless gas, slightly heavier than air.
2. Soluble in water, 4.7 cc in 100 ml at 20°C.

- Nitogen trioxide, N_2O_3.

1. A dark blue liquid boiling at 3.5°C.

- Nitrogen dioxide, NO_2.

1. It associates or decomposes with change in temperature.

$$\underset{\text{(colorless)}}{N_2O_4} \quad \overset{0\text{-}140^\circ}{\leftrightarrow} \quad \underset{\text{(deep brown)}}{2\ NO_2.} \quad \overset{150\text{-}620^\circ}{\leftrightarrow} \quad \underset{\text{(colorless)}}{2\ NO + O_2}$$

2. A poisonous gas with a disagreeable odor.
3. Somewhat soluble in water.

- Nitrogen pentoxide, N_2O_5.

1. A white solid that readily sublimes.

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XVI.8.4. Chemical Properties

- Nitrous oxide, N_2O.

1. Glowing splints, phosphorus, and sulfur burn in nitrous oxide.

$$C + 2\ N_2O \rightarrow CO_2 + 2\ N_2$$

$$S + 2\ N_2O \rightarrow SO_2 + 2\ N_2$$

$$2\ P + 5\ N_2O \rightarrow P_2O_5 + 5\ N_2$$

- Nitric oxide, NO.

1. It combines with oxygen forming nitrogen dioxide.

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

2. It supports the burning of wood or phosphorus but not sulfur or candles.

- Nitrogen trioxide, N_2O_3.

1. It reacts with water to form nitrous acid.

$$N_2O_3 + H_2O \rightarrow 2\ HNO_2$$

- Nitrogen dioxide, NO_2.

1. It reacts with water to form nitric acid and nitrous acid.

$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

- Nitrogen pentoxide, N_2O_5.

1. It reacts with water to form nitric acid.

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$

XVI.8.5. Uses

- Nitrous oxide, N_2O.

1. In dentistry and surgery it is administered with oxygen as an anesthetic. (Laughing gas.)

- Nitric oxide, NO.

1. An intermediate product in the manufacture of nitric acid by the Arc process.
2. As a catalyst in the lead-camber process for making sulfuric acid.

- Nitrogen trioxide, N_2O_3.

1. Important as the anhydride of nitrous acid.

- Nitrogen dioxide, NO_2.

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1. Manufacture of nitric acid.
2. Catalyst in the lead-chamber process for making sulfuric acid.
3. Small quantities for bleaching flour.

- Nitrogen pentoxide, N_2O_5.
  1. Important as the anhydride of nitric acid.

XVI.8.6. NITRIC ACID, HNO_3

XVI.8.6.1. Introduction

- Nitric acid was formerly known as "aqua fortis," strong water, to the alchemists.

XVI.8.6.2. Preparation

- By heating a nitrate with sulfuric acid.

$$NaNO_3 + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HNO_3 \uparrow$$

- By the oxidation of ammonia in the presence of platinum.

$$4\ NH_3 + 5\ O_2 \rightarrow 6\ H_2O + 4\ NO$$

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

- From nitric oxide formed by the direct union of the elements.

$$N_2 + O_2 \rightarrow 2\ NO$$

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$

XVI.8.6.3. Physical Properties

- It is a colorless, fuming liquid.
  1. Dissociation products, principally NO_2, may color it yellow.
- It forms a constant boiling mixture with water, containing 68% hydrogen nitrate at 121°C, and 760 mm pressure.
- Specific gravity, 1.54. Boiling point, 86°C.

XVI.8.6.4. Chemical Properties

- It is unstable in sunlight.

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$$HNO_3 \leftrightarrow 2\ H_2O + 2\ N_2O_5 \leftrightarrow 2\ H_2O + 4\ NO_2 + O_2$$

- Concentrated nitric acid acts predominantly as an oxidizing agent.

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$$

$$C + 4\ HNO_3 \rightarrow 4\ NO_2 + CO_2 + 2\ H_2O$$

- Dilute nitric acid acts predominantly as a strong acid.

$$HNO_3 \leftrightarrow H^+ + NO_3^-\text{, or}$$

$$HNO_3 + H_2O \leftrightarrow H_3O^+ + NO_3^-$$

- It reacts with hydrochloric acid (aqua regia), to dissolve even gold and platinum..

$$2\ HNO_3 + 6\ HCl \rightarrow 4\ H_2O + 2\ NO\uparrow + 3\ Cl_2\uparrow$$

$$Au + HCl + NO_3^- \rightarrow AuCl_4^- + NO + 2\ H_2O$$

XVI.8.6.5. Uses

- *Fertilizers* are prepared by the use of nitric acid. Such fertilizers supply necessary nitrogen to the growing crops.
- *Explosives* such as dynamite, smokeless powder, T.N.T., nitroglycerine, and picric acid are made by the use of nitric acid.
- *Perfumes, dyes,* and *medicinals* from coal tar are made by the use of nitric acid.
- *Pyroxylin* used in preparation of photographic films and celluloid.
- *Sulfuric acid* utilizes nitric acid and the oxides of nitrogen as a catalyst in the lead-chamber process.
- *Laboratory reagent* of considerable importance.

XVI.8.6.6. Analytical Test

- Nitrates are usually detected by the addition of ferrous sulfate to the unknown, and then by the cautions addition of concentrated sulfuric acid, forming two distinct layers.
    1. A brown ring develops at the junction of the two liquids due to the formation of the complex ion, $Fe(NO)^{++}$.
    2. The test is not satisfactory in the presence of chlorates, iodates, bromides, nitrites, ferrocyanides, or ferricyanides.

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XV.18.7. NITROUS ACID, HNO_2

XVI.8.7.1. Introduction

- Nitrous acid, HNO_2, has never been isolated in a pure condition.
- Its presence and formula are inferred from the properties of its salts..

XVI.8.7.2. Preparation

- By the action of equal volumes of nitric oxide, NO, and nitrogen dioxide, NO_2, on water..

$$NO + NO_2 + H_2O \leftrightarrow 2\ HNO_2$$

- By treating a nitrite with dilute sulfuric or hydrochloric acid..

$$NaNO_2 + HCl \rightarrow NaCl + HNO_2$$

XVI.8.7.3. Physical Properties

- A slight bluish color in solution.

XVI.8.7.4. Chemical Properties

- Its reacts with urea liberating nitrogen and carbon dioxide..

$$CO(NH_2)_2 + 2\ HNO_2 \rightarrow 3\ H_2O + CO_2\ \uparrow + 2\ N_2\ \uparrow$$

- Amino nitrogen in proteins is determined by treating the compound with nitrous acid and measuring the nitrogen evolved. (Van Slyke method.).

$$CH_2(NH_2)COOH + HNO_2 \rightarrow CH_2(OH)COOH + H_2O + N_2\ \uparrow$$

- It may react as an oxidizing agent.

$$2\ HNO_2 + 2\ HI \rightarrow 2\ H_2O + I_2 + 2\ NO$$

- It may act as a reducing agent.

$$5\ HNO_2 + 2\ KMnO_4 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 3\ H_2O + 5\ HNO_3$$

XVI.8.7.5. Uses

- Dyes are frequently prepared by the use of nitrous acid, formed from sodium nitrite and another acid..

XVI.8.7.6. Analytical Test

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- Nitrites are distinguished from nitrates by the fact that the ferrous ion is oxidized in dilute acetic acid by nitrites but not by nitrates, to give the characteristic brown color of the $Fe(NO)^{++}$ ion.

XVI.8..8. Fixation of atmospheric nitrogen

XVI.8.1. Definition

- Nitrogen fixation is any method by which the nitrogen of the air can be combined with one or more elements so as to make it available for plant life and industrial uses.

XVI.8..2. Natural Methods

- Bacteria.
  1. Bacteria attached to the roots of certain leguminous plants, clover, alfalfa, cow-peas, and soy beans, have the ability to absorb nitrogen from the air and make it available for growing plants.
- Lightning.
  1. Nitric oxide from the nitrogen and oxygen of the air is produced by every lightning flash.
  2. This in turn is converted into nitric acid by the excess oxygen of the air and the rain.

XVI.8..3. Commercial Methods

- Haber Process.
  1. Nitrogen and hydrogen combine directly to form ammonia at pressure of 200 to 1,000 atmospheres in the presence of platinum, mixtures of iron and molybdenum, or iron in association with potassium oxide and aluminium oxide.
  2. The nitrogen is usually obtained from liquid air and the hydrogen from water gas.
  3. Temperatures of 400° to 600° are generally used
  4. The ammonia produced may be dissolved in sulfuric acid forming ammonium sulfate or may be oxidized to form nitric acid
  5. Equations:

$$N_2 + 3\,H_2 \xrightarrow{\text{catalyst}} 2\,NH_3$$

$$2\,NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

$$4\,NH_3 + 5\,O_2 \rightarrow 6\,H_2O + 4\,NO$$

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$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

- Cyanamide Process.
    1. Limestone is heated with coke in an electric furnace to produce calcium carbide, CaC_2.
    2. The carbide is then heated with nitrogen at white heat to form calcium cyanamide, $CaCN_2$.
    3. This is treated in an autoclave with steam to produce ammonia.
    4. Equations:

$$CaCO_3 + 4\ C \rightarrow CaC_2 + 3\ CO$$

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

$$CaCN_2 + 3\ H_2O \rightarrow CaCO_3 + 2\ NH_3\ \uparrow$$

- Arc Process.
    1. Oxygen and nitrogen combine somewhat at temperatures around 2,000°C, in an electric arc.
    2. The yield seldom exceeds 2.5 %.
    3. The nitric oxide is converted into nitric acid or nitrates.
    4. Equations:

$$N_2 + O_2 \rightarrow 2\ NO$$

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

- Nitride Process.
    1. Certain metallic nitrides react with steam to produce ammonia.
    2. The process is of little commercial importance.
    3. Equations:

$$N_2 + 2\ Al \rightarrow 2\ AlN$$

$$2\ AlN + H_2O \rightarrow Al(OH)_3 + NH_3$$

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THE PHOSPHORUS FAMILY

1. Introduction

- The phosphorus or nitrogen family of elements includes nitrogen, phosphorus, arsenic, antimony, and bismuth.
- This series of elements appears in column five of the periodic table.

XVI.9.2. Common Characteristics

- Have maximum positive valence of five
- All except bismuth have a negative valence of three.
- Become more metallic with increasing atomic weight.
- All form acidic pentoxides, X_2O_5, although the acidic properties decrease with increasing atomic weight.
- All except bismuth exist in more than one allotropic form.
- Density increases with increasing atomic weight.
- They all combine with oxygen and the halogens.
- Their halides are easily hydrolyzed.

XVI.9.3. Phosphorus

XVI.9.3.1. Historical

- Discovered in 1669 by Brand from urine while looking for the Philosopher's Stone.
- Name "phosphorus" means "light bearing."

XVI.9.3.2. Occurrence in Combination Only

- Phosphate rock or calcium phosphate, $Ca_3(PO_4)_2$.
  1. Found in Florida, Tennessee, Montana, and northern Africa.
- Apatite or calcium flouphosphate, $Ca_5(PO_4)_3F$.
  1. Found in South Carolina, Canada, and Spain.
- Phosphoproteins of the brain and nervous tissues of animals, and in plants.
- Bones and teeth of animals.

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9.3.3. Commercial Preparation

- In electric furnaces from phosphate rock, sand, and powdered coke.

1. $Ca_3(PO_4)_2 + 3\ SiO_2 \rightarrow 3\ CaSiO_3 + P_2O_5$

$$P_2O_5 + 5\ C \rightarrow 5\ CO + P_2 \uparrow$$

2. The free phosphorus distills and is condensed in cold water.

XVI.9.3.4. Allotropic Forms of Phosphorus

- White phosphorus.
  1. A waxy solid, insoluble in water, soluble in carbon disulfide.
  2. Poisonous and spontaneously inflammable.
  3. Stored and handled under water.
- Red phosphorus.
  1. A red semi-crystalline solid.
  2. The stable form of phosphorus.
  3. Non-poisonous. Less soluble.
- Violet phosphorus.
  1. Prepared by crystallization of phosphorus from molten lead.
- Black phosphorus.
  1. Formed at 2000°C, and 4,000 atmospheres pressure.

XVI.9.3.5. Physical Properties

- Atomic weight, 30.974. Atomic number, 15.
- Melting point, 44.1°C. Boiling point, 280°C.
- Density: White 1.82, red 2.20.
- Solubility: White, insoluble in water, soluble in carbon disulfide. Red, insoluble in water and carbon disulfide.
- White variety changes to red by light, or heating to 250°C in the absence of air.
- Red variety changes to white by vaporization and sudden cooling.

XVI.9.3.6. Chemical Properties

- Valence, negative 3, and positive 1, 3, and 5.
- Phosphorus combines with non-metals, *e.g.*,

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$$4\ P + 3\ O_2 \rightarrow 2\ P_2O_3 \qquad \text{or} \qquad 4\ P + 5\ O_2 \rightarrow 2\ P_2O_5$$

$$2\ P + 3\ I_2 \rightarrow 2\ PI_3$$

$$2\ P + 5\ Cl_2 \rightarrow 2\ PCl_5$$

XVI.9.3.7. Uses

- White phosphorus.
  1. Smoke screens in warfare.
  2. Rat poison and pastes, mixed with flour and lard.
  3. Preparation of P_4S_3 for the match industry.
- Red phosphorus.
  1. Match industry.

XVI.9.3.8. Analytical Test

- Traces in food oxidized with HNO_3 to H_3PO_4.
- Soluble phosphate fertilizers and salts are extracted with water.
- Ammonium molybdate reagent is added and the solution (containing nitric acid) is warmed.
- A yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$, is formed.

XVI.9.3.9. Phosphorus Compounds

⇒ Phosphorus pentoxide, P_2O_5.

1. Prepared bu burning phosphorus in air.

$$4\ P + 5\ O_2 \rightarrow 2\ P_2O_5$$

2. It is anhydride of the phosphoric acids, *e.g.*,

$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4$$

3. A very convenient and powerful drying agent.

⇒ Phosphine, PH_3.

1. Prepared by boiling phosphorus with alkalies, or the action of water on calcium phosphide.

$$4\ P + 9\ KOH \rightarrow 3\ K_3PO_2 + 3\ H_2O + PH_3 \uparrow$$

$$Ca_3P_2 + 6\ H_2O \rightarrow 3\ Ca(OH)_2 + 2\ PH_3 \uparrow$$

2. Phosphine usually contains a trace of P_2H_4 and P_4H_2 which makes it spontaneously combustible.

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⇒ Phosphorus acid (ortho), H_3PO_3.

1. Prepared by action of P_2O_3 and water.

$$P_2O_3 + 3\ H_2O \rightarrow 2\ H_3PO_3$$

⇒ Phosphoric acid and their preparation.

1. Metaphosphoric acid, HPO_3.

$$P_2O_5 + H_2O \rightarrow 2\ HPO_3 \qquad \text{or}$$

$$H_3PO_4 \xrightarrow{\Delta} HPO_3 + H_2O\uparrow$$

2. Pyrophosphoric acid, $H_4P_2O_7$.

$$P_2O_5 + 2\ H_2O \rightarrow H_4P_2O_7 \qquad \text{or}$$

$$2\ H_3PO_4 \xrightarrow{250°C} H_4P_2O_7 + H_2O$$

3. Orthophosphoric acid, H_3PO_4.

$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4$$

⇒ Superphosphate of lime, $CaH_4(PO_4)_2$.

1. Used as a fertilizer and in phosphate baking powder.
2. Prepared by action of sulfuric acid on phosphate rock.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \rightarrow 2\ CaSO_4\downarrow + CaH_4(PO_4)_2$$

⇒ Disodium phosphate, Na_2HPO_4.

1. Used as a laboratory reagent and in medicine.
2. Other sodium phosphates are NaH_2PO_4 and Na_3PO_4.

⇒ Microcosmic salt, $Na(NH_4)HPO_4$.

1. Used in analytical work for bead tests.

XVI.9.3.10. The Match Industry

- "Strike Anywhere" matches.
  1. Tip of P_4S_3 which is easily ignited.
  2. Head contains S, rosin, or Sb_2S_3 and an oxidizing agent as PbO_2 or $KClO_3$ and glue.
  3. Stick dipped in paraffin.
  4. Stick treated with ammonium phosphate to prevent "after glow."
- Safety matches.
  1. Head of S or Sb_2S_3 with a little oxidizing agent as $KClO_3$ or $K_2Cr_2O_7$, powdered glass and glue.
  2. Side of box coated with red phosphorus, $KClO_3$ or PbO_2, powdered glass and glue.
  3. Match ignited on side of box.

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XVI.9.4. Arsenic

XVI.9.4.1. Occurrence

- Occasionally found free.
- In combination with many metals, *e.g.*,.

  1. Arsenicalpyrites (mispickel), FeAsS.

- In combination with sulfur, *e.g.*,.

  1. Orpiment, As_2S_3 and realgar, As_2S_2.

XVI.9.4.2. Preparation

- Roasting of sulfide ores and subsequent reduction with carbon.

$$2\ As_2S_3 + 9\ O_2 \xrightarrow{\Delta} 2\ As_2O_3 + 6\ SO_2 \uparrow$$

$$As_2S_3 + 3\ C \xrightarrow{\Delta} 2\ As + 3\ CO \uparrow$$

- Heating arsenal pyrites.

$$FeAsS \rightarrow FeS + As \uparrow$$

XVI.9.4.3. Physical Properties

- A steel-gray, very brittle, crystalline, semimetallic solid.
- Atomic weight, 74.92. Atomic number, 33.
- Sublimes at 500°C, under pressure.
- Boiling point, 615°C.
- Specific gravity, 5.73.
- Two allotropic forms are known, a gray and a yellow.

XVI.9.4.4. Chemical Properties

- Valence, negative 3, and positive 2, 3, and 5.
- All the soluble arsenic compounds are extremely poisonous. (Antidote is colloidal ferric hydroxide.)
- Combines readily with oxygen, the halogens and certain metals, *e.g.*,

$$4\ As + 3\ O_2 \rightarrow 2\ As_2O_3$$

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$$2\ As + 3\ Cl_2 \rightarrow 2\ AsCl_3$$

$$2\ As + 3\ Zn \rightarrow Zn_3As_2$$

XVI.9..4.5. Uses

- Hardening and improving the sphericity of shot.
- Preparation of brass, certain bronzes and pyrotechny.

XVI.9.4.6. Analytical Test

- Both arsenites and arsenates give a yellow precipitate of As_2S_3 with H_2S in hot acid solution.
- Arsenates produce a chocolate brown precipitate of silver orthoarsenate with silver nitrate solution..
- The Marsh test.

1. Consists of the reduction of arsenic compounds with zinc and an acid to arsine, AsH_3.

$$HAsO_2 + 5\ Zn + 10\ HCl \rightarrow 5\ ZnCl_2 + 2\ H_2O + 2\ H_2 + AsH_3 \uparrow$$

2. Arsine is decomposed by heat and the arsenic is deposited as a dark brown or black mirror on a cold object.
3. As little as 0.1 mg of arsenic can be detected.
4. Antimony gives a similar test but is insoluble in a hypochlorite solution.

XVI.9.4.7. Arsenic Compounds

⇒ White arsenic, As_2O_3.

1. Produced by burning arsenic in air.
2. Dissolves in dilute alkalies to form arsenites, *e.g.*,

$$As_2O_3 + 2\ NaOH \rightarrow 2\ NaASO_2 + H_2O$$

3. Used extensively in making insecticides, fusible glass, and decorative white enamels.

⇒ Paris Green, $Cu_3(AsO_3)_2 \cdot Cu(C_2H_3O_2)_2$, and lead arsenate, $Pb_3(AsO_4)_2$.

1. Used as insecticide in combating leaf-devouring insects.

⇒ Arsine, AsH_3 (See Marsh test above.)

⇒ Orthoarsenic acid, H_3AsO_4.

1. Obtained by evaporating a solution of arsenic trioxide in nitric acid.

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2. Resembles orthophosphoric acid in properties.

XVI.9..5. Antimony

XVI.9.5.1. Occurrence

- Occasionally found free.
- From stibnite, Sb_2S_3, and associated with gold, silver and lead.
- China, Mexico, and Bolivia are the principal producers.

XVI.9.5.2. Preparation

- Roasting of sulfide ores and subsequent reduction with carbon or iron.

$$2\ Sb_2S_3 + 9\ O_2 \xrightarrow{\Delta} 2\ Sb_2O_3 + 6\ SO_2 \uparrow$$

$$Sb_2O_3 + 3\ C \xrightarrow{\Delta} 2\ Sb + 3\ CO \uparrow \quad \text{or}$$

$$Sb_2S_3 + 3\ Fe \xrightarrow{\Delta} 3\ FeS + 2\ Sb$$

XVI.9..5.3. Physical Properties

- An extremely brittle, flaky, crystalline, blue-white metal.
- Atomic weight, 121.75. Atomic number, 51.
- Melting point, 630°C. Boiling point, 1635°C.
- Specific gravity, 6.68 at 25°C.
- Expands on solidifying.
- Exists in allotropic forms similar to arsenic.

XVI.9..5.4. Chemical Properties

- Valence, negative 3, and positive 3, and 5.
- Properties are predominantely metallic.
- No reaction with air at room temperature but burns brilliantly when heated.

$$2\ Sb + 3\ O_2 \rightarrow 2\ Sb_2O_3$$

- Combines with the halogens readily.

$$2\ Sb + 3\ Cl_2 \rightarrow 2\ SbCl_3$$

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- Salts are readily hydrolyzed.

$$SbCl_3 + H_2O \rightarrow SbOCl + 2\ HCl$$

XVI.9.5.5. Uses

- Type metal and babbitt.
- Toughen and harden lead for storage-battery grids, pipes, and gutters.

XVI.9.5.6. Analytical Test

- Precipitates as an orange sulfide, Sb_2S_3, with H_2S in acid solution.

XVI.9.5.7. Antimony Compounds

⇒ Tartar emetic, $K(SbO)C_4H_4O_6$.

1. Used in medicine.

⇒ Antimony sesquisulfide, Sb_2S_3.

1. Used in match industry.

⇒ Antimony trichloride, $SbCl_3$.

1. Important laboratory reagent.
2. Used to limited extent in medicine as "butter of antimony."

⇒ Antimony hydroxide, $Sb(OH)_3$.

1. This compound is amphoteric, that is it has both acidic and basic properties.

$$Sb(OH)_3 + 3\ HCl \rightarrow SbCl_3 + 3\ H_2O$$

$$Sb(OH)_3 + 3\ NaOH \rightarrow Na_3SbO_3 + 3\ H_2O$$

XVI.9.6. Bismuth

XVI.9.6.1. Occurrence

- Generally found free.
- Found also as sulfide, oxide, and carbonate in Bolivia.

XVI.9.6.2. Preparation

- By melting out the free metal from its ore.
- Reduction of the sulfide or oxide with carbon or iron.

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- Recovered as a by-product in lead smelting.

XVI.9.6.3. Physical Properties

- A white, crystalline, brittle metal with a slight pinkish tinge. Only one allotropic form known.
- Atomic weight, 208.980. Atomic number, 83.
- Melting point, 271°C. Boiling point, 1450°C.
- Specific gravity, 9.78 at 20°C.
- Expands on solidifying.

XVI.9.6.4. Chemical Properties

- Valence, positive 2, 3, 4, and 5.
- Bismuth is exclusively metallic, and comparatively inactive.
- Bismuth forms sulfates, acetates, carbonates, nitrates, etc.
- It burns at elevated temperatures to the oxide.

$$4\ Bi + 3\ O_2 \rightarrow 2\ Bi_2O_3$$

- Combines slowly with the halogens.

$$2\ Bi + 3\ Cl_2 \rightarrow 2\ BiCl_3$$

- Bismuth salts are readily hydrolyzed.

$$Bi(NO_3)_3 + H_2O \rightarrow BiONO_3 + 2\ HNO_3$$

XVI.9.6.5. Uses

- Low melting alloys for fire plugs, automatic fire sprinklers, electric fuses, auromatic fire alarms, and closing fire-doors.
- Stereotype metal.

XVI.9.6.6. Analytical Test

- Precipitated as a dark sulfide, Bi_2S_3, with H_2S in acid solution.
- May be precipitated and weighed as the oxychloride, BiOCl.
- May be precipitated as the hydroxide, $Bi(OH)_3$ and weighed as the oxide, Bi_2O_3.

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XVI.9.6.7. Bismuth Compounds

⇒ Bismuth subnitrate, $Bi(OH)_2NO_3$ and basic carbonate.

1. Employed in medicine in treating infections of the alimentary canal.

⇒ Sodium bismuthate, $NaBiO_3$.

1. A powerful reducing agent used for laboratory purposes.

XVI.10. Silicon and boron

XVI.10.1. Occurrence of Silicon

- Never occurs free.
- Forms 25.8% of the earth.
- As silica, SiO_2, familiar forms of which are quartz, sand, agate, flint, amethyst, jasper, onyx, and opal
- Silicates or salts of orthosilicic acid and metasilicic acids.
  1. Feldspar, $KAlSi(SiO_4)_2$.
  2. Clay (kaolinite), $H_4Al_2Si_2O_9$.
  3. Mica, $H_2KAl_3(SiO_4)_3$.
  4. Asbestos, $Mg_2Fe_2SiO_4$.

XVI.10.2. Preparation

- Reduction of silicon dioxide with carbon in an electric furnace.

$$SiO_2 + 2\ C \xrightarrow{\Delta} Si + 2\ CO$$

- Reduction of silicon halides by alkali metals.

$$SiCl_4 + 4\ Na \rightarrow Si + 4\ NaCl$$

- Reduction of silicon dioxide with magnesium or aluminium.

$$SiO_2 + 2\ Mg \rightarrow 2\ MgO + Si$$

XVI.10.3. Physical Properties

- Atomic weight, 28.09. Atomic number, 14.
- Melting point, 1420°C. Boiling point, 2600°C.

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- There are two allotropic forms of silicon, a gray semi-metallic form and an amorphous form.

XVI.10.4. Chemical Properties

- Valence of four.
- Silicon resembles carbon in its ability to form hydrides.
- Silicon resembles boron in the reaction of its oxides with basic oxides.
- Silicon burns slowly in air.

$$Si + O_2 \rightarrow SiO_2$$

- Silicon combines with halogens, spontaneously with fluorine, at 300-350° with chlorine, at 500° with bromine, and at red heat with iodine.
- Silicon dissolves in sodium hydroxide solution, liberating hydrogen.

$$Si + 2\ NaOH + H_2O \rightarrow Na_2SiO_3 + 2\ H_2$$

- Silicon is oxidized by steam.

$$Si + 2\ H_2O \xrightarrow{\Delta} SiO_2 + 2\ H_2$$

- Silicon reacts with nitric acid and hydrofluoric acid to produce silicon tetrafluoride.

$$3\ Si + 4\ HNO_3 + 12\ HF \rightarrow 3\ SiF_4 + 4NO + 8\ H_2O$$

- Silicon combines with nitrogen, sulfur, and many metals at high temperatures.

$$3\ Si + 2\ N_2 \rightarrow Si_3N_4$$

$$Si + 2\ S \rightarrow SiS_2$$

$$Si + Fe \rightarrow FeSi$$

XVI.10.5. Uses

- For preparing acid resisting alloys as duriron whcih contains 16% silicon
- For preparing ferrosilicon, FeSi, which is used as a deoxidizing agent in the steel industry.

XVI.10.6. Compounds of Silicon

⇒ Silicon dioxide, SiO_2.

1. Used in the preparation of quartz glass for lenses, prisms, laboratory ware, and windows.

(a) Has a very low coefficient of expansion so it can withstand sudden changes in temperature without breaking.

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(b) It readily transmits ultra-violet light.

2. Dissolves in hydrofluoric acid.

$$SiO_2 + 4\ HF \rightarrow SiF_4 + 2\ H_2O$$

⇒ Silicic Acids, (Ortho - H_4SiO_4, and Meta - H_2SiO_3).

1. Prepared by the action of alkalies on silicon dioxide followed by treatement with an acid.

$$SiO_2 + 4\ NaOH \rightarrow Na_4SiO_4 + 2\ H_2O$$

$$Na_4SiO_4 + 4\ HCl \rightarrow 4\ NaCl + H_4SiO_4$$ (Orthosilicic acid)

$$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2 \uparrow$$

$$Na_2SiO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2SiO_3$$ (Metasilicic acid)

2. These acids are colloidal in nature and are easily dehydrated forming amorphous silicon dioxide, (silica gel).

(a) These gels have high absorbent powers.

(b) Make suitable supports for many catalysts.

⇒ Silicon carbide, (Carborundum), SiC.

1. Prepared from a mixture of sand, coke, sawdust and salt in huge electric furnaces.

$$SiO_2 + 3\ C \xrightarrow{\Delta} SiC + 2\ CO \uparrow$$

2. Used extensively as an abrasive.

⇒ Ferrosilicon carbide, FeSi.

1. Used to prepare iron with high acid resistance, high magnetic permeability, and as a deoxidizing agent in the steel industry.

⇒ Silicon silicate, (Water glass).

1. Prepared by fusing sand with sodium carbonate and charcoal, and then extracting with sodium hydroxide.
2. Solid in concentrated solution as a syrupy liquid.
3. Used as a filler in cheap soaps, washing powders, fireproofing materials, paper sizing, egg-preservative, mineral glue, and waterproofing concrete.

⇒ Hydrogenite.

1. It is a mixture of ferrosilicon and sodium hydroxide.
2. It reacts with water, liberating hydrogen for ballons and air ships.

⇒ Silicon tetrachloride, $SiCl_4$.

1. Prepared by action of chlorine on silicon carbide.

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$$SiC + 2\ Cl_2 \rightarrow SiCl_4 + C$$

2. Also prepared by the action of chlorine on a hot mixture of sand and carbon.

$$SiO_2 + 2\ C + 2\ Cl_2 \rightarrow SiCl_4 + 2\ CO$$

3. Mixtures of silicon tetrachloride and ammonia are used for military smoke screens.

$$SiCl_4 + 4\ H_2O \rightarrow H_4SiO_4 + 4\ HCl$$

$$HCl + NH_3 \rightarrow NH_4Cl$$

$\Rightarrow$ Silicon hydrides.

1. The first 8 members of the series, Si_nH_{2n+2}, corresponding to the paraffin series are known.
2. They are unstable and inflamable spontaneously in air.

XVI.10.7. Analytical Test

- Silicon is precipitated and weghed as silicon dioxide, SiO_2.
- Silicon liberates SiF_4 when treated with HF.

XVI.10.8. The glass industry

XVI.10.8.1. Definition

- Glass is a fused non-crystalline mass of basic oxides and silicon dioxide.
- Among the basic oxides that may be present are Na_2O, CaO, K_2O, Al_2O_3, Bi_2O_3, PbO, ZnO, Sb_2O_3, and As_2O_3.

XVI.10.8.2. Preparation

- Common *soda*glass is prepared from sand, limestone and sodium carbonate, *e.g.*,

$$6\ SiO_2 + CaCO_3 + 2\ Na_2CO_3 \xrightarrow{\Delta} Na_4CaSi_6O_{15} + 3\ CO_2$$

- Percentage composition is approximately, SiO_2, 71-78; Na_2O, 12-17; CaO, 5-15; and Al_2O_3, 1-4.

XVI.10.8.3. Types of Glass

- *Hard glass, Bohemian glass*, or *Potash glass* contains K_2O.
- *Flint* or potash-lead glass is used in making cut glass articles.

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- *Pyrex*glass for laboratory and kitchen use has a high content of SiO_2 (80%), B_2O_3 (12%), and the balance Na_2O and Al_2O_3.
- *Jena*glass is a zinc, barium, boron silicate.

XVI.10.8.4. Manufacture of Glass Articles

- Window glass is blown.
- Bottles, etc, are blown in molds.
- Plate glass is rolled and polished.
- All glass articles must be carefully annealed.

XVI.10.8.5. Colored Glass

- Greenish color of cheap bottles is due to iron.
- Chromium produces a rich green.
- Colloidal gold gives a ruby red.
- Selenium produces a red coloration.
- Copper and cobalt produce a blue.
- Manganese gives a pink to violet color.
- Silver produces a yellow glass.
- Iron and manganese give a yellow to brown color.
- Calcium fluoride yields a white translucent appearance.

XVI.10.8.6. Enamels

- Enamels are essentially glasses of special composition.
- Must be free of poisonous components.
- Must have approximate coefficient of expansion of the metal or alloy to which they are attached.
- Enameled bath tubs and sinks are cast iron that has been coated with a white lead glass.

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XV.10.9. BORON

XV. .9.1. Occurrence

- Constitutes only 0.001% of the earth's crust.
- As magnesium borates in Stassfurt deposits of Germany.
- As colemanite, $Ca_2B_6O_{11}\cdot 5H_2O$, and borax, $Na_2B_4O_7\cdot 10H_2O$,. in the arid regions of the western United States.
- Deposits have resulted from the evaporation of inland seas.

XVI.10.9.2. Preparation

- By the reduction of the oxide with powdered magnesium or sodium.

$$B_2O_3 + 3\ Mg \rightarrow 3\ MgO + 2\ B$$

XVI.10.9.3. Physical Properties

- It is a dark brown powder,or when fused it is almost as hard as a diamond.
- Atomic weight, 10.81. Atomic number, 5.
- Melting point, 2000-2500°C. Sublimes at 2550°C.
- Boron as an element has no commercial uses of importance.

XVI.10.9.4. Chemical Properties

- Valence, negative 3, and positive 3.
- Boron burns with a green flame.

$$4\ B + 3\ O_2 \rightarrow 2\ B_2O_3$$

- It combines with the halogens, *e.g.*,

$$2\ B + 3\ Cl_2 \rightarrow 2\ BCl_3$$

- It dissolves in alkalies forming borates, *e.g.*,

$$2\ B + 6\ KOH \rightarrow 2\ K_3BO_3 + 3\ H_2$$

- Nitric acid oxidizes boron to boric acid.

$$B + HNO_3 + H_2O \rightarrow H_3BO_3 + NO$$

- It combines with many metals to form borides, *e.g.*,

$$2\ B + 3\ Zn \rightarrow Zn_3B_2$$

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XVI.10.9.5. Compounds of Boron

⇒ Borax, $Na_2B_4O_7$.

1. Purified by crystallization of natural deposits.
2. Prepared by the reaction of boric acid with sodium carbonate.

$$4\ H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6\ H_2O + CO_2\ \uparrow$$

3. Uses.
   (a) Extensively for metallic bead tests in analytical work.
   (b) As a flux in soldering and welding.
   (c) Preparation of.pigments and gems
   (d) Manufacture of glass, enamels, and soap.
   (e) Sizing for paper.
   (f) Preservative for wood and meats.
   (g) Softening water.

⇒ Boric acid, H_3BO_3.

1. Prepared by treating borax with sulfuric acid.

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \rightarrow 4\ H_3BO_3 + Na_2SO_4$$

2. Only slightly soluble in water forming a weakly acid solution.
3. Used as a mild antiseptic in powders, and in solution for eye wash.

⇒ Boron Carbide, CB_6.

1. An extremely hard abrasive.
2. Used extensively to resist wear by friction in textile mills, etc.

XVI.10.9.6. Analytical Test

- Boron compounds when burned with methanol (CH_3OH), in the presence of sulfuric acid produce a prominent green flame.
- Boric acid may be titrated, using phenolphtalein as an indicator, in presence of glycerol or mannite.

XVI.11. Carbon and the oxides of carbon

XVI.11.1. Occurrence

- Free carbon in coal, graphite, and diamonds.
- Chemically combined.

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1. Carbonates as limestone, dolomite, marble, etc.
2. Carbohydrates, fats and proteins of plants and animals.
3. Carbon dioxide of the air.

XVI.11.2. Allotropic Forms of Carbon

- Diamonds.
  1. A dense, transparent, crystalline form of carbon.
  2. Produced principally in South Africa.
  3. Hardest substance known. Density, 3.51.
  4. Used for jewelry, rock drills, phonograph needles, and an abrasive.
  5. At red heat diamonds turn to graphite and burn to carbon dioxide in oxygen.
- Graphite.
  1. A soft, grayish-white crystalline form of carbon.
  2. Density, 2.50.
  3. Found naturally in Siberia, Ceylon, and New York, or manufactured from coke or anthracite coal in electric furnaces.
  4. It is a conductor of electricity.
  5. Used for electrodes, arc light carbons, as a lubricant, pencil-leads, crucibles, and stove polish.
- Amorphous carbon.
  1. Coke.
     (a) Prepared by the destructive distillation of soft coal.
     (b) By-products are coal gas, ammonia, and coal tar.
     (c) Coke contains 80 to 95% carbon.
     (d) Used as reducing agent in the iron and steel industry, for fuel, and making water gas.
  2. Charcoal.
     (a) Prepared by the destructive distillation of wood.
     (b) By-products and combustible gases, acetic acid, and methanol (CH_3OH).
     (c) Charcoal contains 95 to 98% carbon.
     (d) Used as reducing agent in the iron and steel industry, blacksmithing, gas masks, and for fuel.
  3. Boneblack.
     (a) Made by charring bones.

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(b) Boneblack contains about 10% carbon, the remainder is calcium phosphate.

(c) Used chiefly in decolorizing sugar and oils.

4. Carbon black.

(a) Prepared by burning natural gas in a limited supply of air.

(b) Used for printer's ink, filler for rubber, black paint, and shoe polish..

5. Lampblack.

(a) Prepared by burning fats or oils in a limited supply of air.

6. Hard coal (Anthracite).

(a) A hard, black, metallic-like substance, with a high kindling temperature.

(b) Mined principally in Pennsylvania.

(c) Contains about 85% carbon.

(d) Used as a fuel, for making water gas, and graphite.

(e) Other forms of coal include bituminous, lignite, and peat.

XVI.11..3. Properties of Carbon

- The various allotropic forms of carbon differ in color, density, and hardness.
- Carbon sublimes at 3600°C, but can not be melted.
- Carbon occupies the first position of column four in the periodic table and possesses 4 velence electrons.
- Atomic weght, 12.011. Atomic number,6.
- Valence, positive 2, 3, 4, and negative 4.
- Insoluble in all common solvents, but dissolves in molten metals.
- Carbon forms covalent compounds in which pairs of electrons are shared.
- Carbon has the usual ability to combine with itself, atom to atom, forming numerous chain and ring compounds. The number of such known carbon compounds exceeds 300,000.
- Carbon is comparatively inert and is not affected by boiling with dilute acids and alkalies.
- At high temperatures carbon combines with oxygen, most metals, and many non-metals, *e.g.*,

$$2\,C + O_2 \rightarrow 2\,CO \qquad \text{or} \qquad C + O_2 \rightarrow CO_2$$

$$C + 3\,Fe \xrightarrow{\Delta} Fe_3C$$

$$C + 2\,Cl_2 \xrightarrow{\Delta} CCl_4C \qquad \text{or} \qquad C + 2\,S \xrightarrow{\Delta} CS_2$$

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- Carbon is an efficient reducing agent, *e.g.*,

$$3C + Fe_2O_3 \xrightarrow{\Delta} 2\,Fe + 3\,CO\uparrow$$

$$3C + CaO \xrightarrow{\Delta} CaC_2 + CO\uparrow$$

$$3C + SiO_2 \xrightarrow{\Delta} SiC + 2\,CO\uparrow$$

XVI.11..4. Analytical Test

- Carbon and organic compounds are readily coverted to carbon dioxide by oxidation.
- When carbon dioxide is bubbled through lime water, $Ca(OH)_2$, a milky white precipitate is formed. This serves as a qualitative test.

$$Ca(OH)_2 + CO_2 \rightarrow H_2O + CaCO_3\downarrow$$

- Carbon dioxide may be absorbed and weighed in "Ascerite."
- Carbonates may be precipitated and weighed as barium carbonate, $BaCO_3$.

XVI.11..5. Inorganic Compounds of Carbon

⇒ Calcium carbide, CaC_2, and acetylene, C_2H_2.

1. Prepared from coke and quick lime in an electric furnace at a temperature of 2800°C.

$$CaO + 3\,C \xrightarrow{\Delta} CaC_2 + CO\uparrow$$

2. Calcium carbide reacts with water, producing acetylene.

$$CaC_2 + 2\,H_2O \xrightarrow{\Delta} Ca(OH)_2 + C_2H_2\uparrow$$

⇒ Carbon disulfide, CS_2.

1. Prepared by passing sulfur vapor over red-hot carbon in the absence of air.

$$C + 2\,S \xrightarrow{\Delta} CS_2$$

2. An extremely volatile liquid (Boiling point 46.3°C).
3. Carbon disulfide has an extremely low kindling temperature and forms dangerously explosive mixtures with air.
4. Used as a solvent, insecticide, and in the manufacture of carbon tetrachloride, CCl_4.

⇒ Carbon cyanamide, $CaCN_2$. (See § XV.24).

⇒ Silicon carbide (Carborundum), SiC. (See § XV.26).

⇒ Carbon tetrachloride, CCl_4.

1. Prepared by the action of chlorine upon carbon disulfide, in the presence of a little iodine.

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$$CS_2 + 3\ Cl_2 \rightarrow S_2Cl_2 + CCl_4$$

2. Carbon tetrachloride is a readily volatile liquid (boiling point 76°C), producing heavy vapors.
3. An excellent solvent for oils, fats, and greases.
4. Used in fire extinguishers ("Pyrene"), dry cleaning("Carbona"), and extracting oily seeds.

XVI.11.6. Carbon monoxide, CO

- Preparation

1. By the burning of carbon in a limited supply of air.

$$2\ C + O_2 \rightarrow 2\ CO$$

2. By the reduction of carbon dioxide with carbon.

$$CO_2 + C \xrightarrow{\Delta} 2\ CO$$

3. By the dehydration of formic or oxalic acids with sulfuric acid. (Laboratory method.)

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO$$

$$H_2C_2O_4 \xrightarrow{H_2SO_4} H_2O + CO_2 + CO$$

4. By the reaction of steam on white hot coke. (Water gas reaction.)

$$C + H_2O \xrightarrow{\Delta} H_2 + CO$$

5. Exhaust of gasoline engines, from coal stoves and furnaces.

- Properties.

1. It is a colorless, odorless, intensely poisonous gas, insoluble in water, and slightly lighter than air.
2. Burns with a pale blue flame.

$$2\ CO + O_2 \rightarrow 2\ CO_2$$

3. It is a powerful reducing agent, *e.g.*,

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

- Uses.

1. As a reducing agent along with carbon.
2. An important component of many fuel gases.
3. Production of synthetic methanol and formaldehyde.

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.7. Carbon dioxide, CO_2

- Occurrence.
  1. In the atmosphere to the extent of 0.03%.
  2. In effervescent mineral waters.
  3. In volcanic gases, certain caves, and form fissures in the earth.
  4. Certain natural gas wells which supply nearly pure carbon dioxide.
- Preparation.
  1. By the action of an acid on a carbonate. (Laboratory method.)

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

  2. By burning carbon or organic compounds in an excess of air.

$$C + O_2 \rightarrow CO_2$$

$$CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2$$

  3. By heating numerous carbonates.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$2\ NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

  4. By alcoholic fermentation of glucose.

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

  5. By the reaction of metallic oxides with carbon or carbon monoxide.

$$Fe_2O_3 + 3CO \xrightarrow{\Delta} 2\ Fe + 3\ CO_2$$

$$SnO_2 + C \xrightarrow{\Delta} Sn + CO_2$$

- Properties.
  1. It is a colorless, odorless, non-poisonous, heavy gas. (1 liter weighs 1.96 g.)
  2. It is easily liquefied and solidified.
  3. It dissolves in and reacts with water forming carbonic acid. (100 g of water dissolves 0.145 g of CO_2 at 25°C.)

$$H_2O + CO_2 \leftrightarrow H_2CO_3$$

  4. Carbon dioxide supports only the combustion of the most active metals.

$$2\ Mg + CO_2 \rightarrow 2\ MgO + C$$

  5. Carbon dioxide is absorbed by plants and produces glucose, starch, and cellulose in the presence of chlorophyll and sunlight.

$$6\ CO_2 + 5\ H_2O \rightarrow (C_6H_{10}O_5)_x + 6\ O_2$$

- Uses.
  1. As leavening agent in bread and cake baking.

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(a) Sour milk containing lactic acid, ($HC_3H_5O_3$), reacts with the baking soda used.

$$NaHCO_3H + HC_3H_5O_3 \rightarrow NaC_3H_5O_3 + H_2O + CO_2 \uparrow$$

(b) Cream of tartar baking powders contain baking soda, potassium acid tartrate, ($KHC_4H_4O_6$), tartric acid, ($H_2C_4H_4O_6$), and starch.

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2 \uparrow$$

$$2\ NaHCO_3 + H_2C_4H_4O_6 \rightarrow Na_2C_4H_4O_6 + 2\ H_2O + 2\ CO_2 \uparrow$$

(c) Phosphate baking powders contain baking soda, calcium acid phosphate, [$CaH_4(PO_4)_2$], and starch.

$$2\ NaHCO_3 + CaH_4(PO_4)_2 \rightarrow Na_2HPO_4 + CaHPO_4 + 2\ H_2O + 2\ CO_2 \uparrow$$

(d) Alum baking powders contain baking soda, an alum, [$NaAl(SO_4)_2$], and starch.

$$3\ NaHCO_3 + NaAl(SO_4)_2 \rightarrow 2\ Na_2SO_4 + Al(OH)_3 + 3\ CO_2 \uparrow$$

2. In household fire extinguishers. Air containing 15% of carbon dioxide will not support combustion.

(a) Dry powder extinguishers contain sand, (SiO_2), and baking soda, ($NaHCO_3$).

$$2\ NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

(b) Baking soda, sulfuric acid type.

$$2\ NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O + 2\ CO_2$$

(c) *Foamite* extinguishers contain solutions of baking soda, ($NaHCO_3$), aluminium sulfate, [$Al_2(SO_4)_3$], and licorice extract.

$$Al_2(SO_4)_3 + 6\ NaHCO_3 \rightarrow 3\ Na_2SO_4 + 2\ Al(OH)_3 \downarrow + 6\ CO_2$$

(d) Compressed carbon dioxide in steel cilinders may be released around burning objects.

(e) "Pyrene" extinguishers contain carbon tetrachloride, a low boiling liquid, that produces a heavy, non-combustible vapor, that excludes oxygen in theair from the burning object and thus extinguishes the flame.

3. The manufacture of carbonated beverages.

4. For refrigeration.

(a) Where the fumes of ammonia or sulfur dioxide may be objectionable, in mechanical refrigeration.

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(b) "Dry ice" or solid carbon dioxide (temperature -79°C) is used for handling fish and ice cream. It is about ten times as efficient as an equal amount of salt and ice.

5. In the Solvay process for preparing baking and washing soda. (See § XV.6.)
6. For the manufacture of white lead. (See § XV.15.)

XVI.12. Fuels

XVI.12.1. Definition

- A *fuel* is a combustible substance that may be burned to produce useful heat, without the production of excessively objectionable by-products
- The heat value, expressed in *calories per gram, joule per gram,* or *British thermal units* can be determined by burning a known quantity of the fuel in a *calorimeter.*
- The original source of all heat, stored in fuels on the earth today, is the sun.

XVI.12.2. Types of Fuels

- Gaseous Fuels.
  1. Natural gas.
     (a) Consists principally of methane, CH_4.
     (b) Comes from wells, principally in oil producing regions.
  2. Coal gas.
     (a) Produced by the destructive distillation of coal.
     (b) The tar, ammonia, and hydrogen sulfide, must be removed by purification before use.
     (c) Contains about 50% hydrogen, 30% methane, and traces of ethylene, carbon monoxide, carbon dioxide, nitrogen, and oxygen.
  3. Water gas.
     (a) Made by passing steam over hot coal or coke.

$$C + H_2O \xrightarrow{\Delta} CO + H_2$$

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(b) Contains 40 to 50% of carbon monoxide, 45 to 50% of hydrogen, 3 to 7% of carbon dioxide, and 4 to 5% of nitrogen.

(c) By *enriching* the water gas with oil vapor, it can be used for illuminating purposes.

(d) It is now the chief source of industrial hydrogen.

4. Producer gas.

(a) Produced by passing a limited supply of air through coke or anthracite coal.

(b) It contains 30 to 40% of carbon monoxide, 60% nitrogen, and 2 to 5% hydrogen.

(c) It is an important by-product of many industrial and metallurgical operations. (Blast furnace gas.)

5. Oil-water gas.

(a) Prepared, where crude oil is cheap, by spraying crude oil and steam upon heated bricks.

(b) It contains methane, ethane, carbon monoxide and hydrogen.

6. Acetylene, C_2H_2.

(a) Prepared by the action of water on calcium carbide.

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

(b) Used extensively for the cutting and welding of metals.

(c) Acetylene is extremely unstable when stored under pressure and may explode with terrific violence. It may be strored safely in solution with acetone, $(CH_3)_2CO$, as the solvent.

- Liquid Fuels.

1. Petroleum.

(a) Petroleum is a complex mixture of numerous hydrocarbons..

(b) It is used as a fuel in steamships, rairoad locomotives, manufacturing plants, and oil burning furnaces in homes.

$$x\ C_nH_{2n+2} + x\ O_2 \rightarrow x\ H_2O + x\ CO_2$$

(c) Gasoline.

1°- Obtained from crude oil by "cracking" and fractional distillation.

2°- Contains hydrocarbon molecules with 6 to 8 carbon atoms each.

3°- Used principally as motor fuel.

(d) Kerosene.

1°- Obtained from crude oil by fractional distillation.

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2°- Contains hydrocarbon molecules with 10 to 16 carbon atoms each.

3°- Used in cook stoves, kerosene lamps, and some internal combustion engines.

2. Alcohol.

(a) Wood alcohol (Methanol), CH_3OH.

1°- Prepared originally by the destructive distillation of wood.

2°- Prepared principally from hydrogen and carbon monoxide with catalysts of zinc oxide and finely divided copper

3°- It burns to produce carbon dioxide and water.

$$2\ CH_3OH + 3\ O_2 \rightarrow 4\ H_2O + 2\ CO_2$$

(b) Denaturated alcohol (Ethanol), C_2H_5OH.

1°- Denaturated alcohol is alcohol that has been rendered unfit or unsafe for beverage purposes.

2°- Cost of alcohol limits its use.

3°- Produces a clean, hot flame. ("Canned heat.")

4°- Used to a limited extent as a substitute for gasoline as a motor fuel.

5°- Burns to produce carbon dioxide and water.

$$C_2H_5OH + 3\ O_2 \rightarrow 3\ H_2O + 2\ CO_2$$

3. Heats of combustion.

(a) Pennsylvania crude oil, 19.505 B.t.u. per lb.

(b) Gasoline, 20.750 B.t.u. per lb.

(c) Kerosene, 19.810 B.t.u. per lb.

(d) Denaturated alcohol, 11.620 B.t.u. per lb.

- Solid Fuels.

1. Anthracite coal, bituminous coal, lignite, peat, coke, and charcoal, burn to produce carbon dioxide or carbon monoxide. (See § XV.27.)

$$C + O_2 \rightarrow CO_2 \quad \text{(Excess of oxygen.)}$$

$$2\ C + O_2 \rightarrow 2\ CO \quad \text{(Excess of carbon.)}$$

2. Wood burns to produce predominantely carbon dioxide and water.

$$(C_6H_{10}O_5)_x + 6x\ O_2 \rightarrow 5_x\ H_2O + 6x\ CO_2$$

XVI.12.3. Flames

- A flame is a zone of burning gas.

1. Gases burn readily when mixed with air.

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2. Liquids vaporize first and the vapors burn.
3. Even solids produce gaseous products to burn with a visible flame.

- Flames naturally present several distinct zones or cones.
  1. An inner cone of unburned gas.
  2. A reducing cone immediately above.
  3. An outer oxidizing cone.
- Luminosity of Flames.
  1. The amount of light produced by flames usually depends upon the presence of glowing solid particles.
  2. Acetylene, C_2H_2, burns with a very luminous flame due to its high carbon content, (92%). A deposit of soot is usually obtained by holding a cool object in a luminous flame.

XVI.13. Some organic compounds

XV.13.1. Introduction

- A study of compounds containing carbon is known as *organic chemistry*.
- Other elements, commonly H, O, N, P, S, Cl, Br, and I, are often associated with carbon in organic compounds.
- There are more than a qurter of a million organic compound known.
- Carbon possesses a unique capacity to combine, atom to atom, forming chains and rings of considerable complexity.
- Organic chemistry involves fundamentally a study of all plant and animal processes and compounds.
- Carbon forms numerous *homologous series* of related compounds, where each differs from the preceding by a constant difference.
- Organic compounds are derived principally from plants, animals, coal, petroleum, natural gas, and oil shale distillates.

XV.13.2. Isomorfism

- *Isomerism* is a condition where two compounds have the same molecular formula but different structural formulas.

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1. Ethyl alcohol, C_2H_5OH, and dimethyl ether, $CH_3 — O — CH_3$, are isomers..
2. Propionic acid, C_2H_5COOH, and methyl acetate, CH_3COOCH_3 are isomers.
3. Isomerism is possible because of the many defferent structures that may be formed with the same number and kind of atoms.

XV.13.3. Hydrocarbons

XV.13.3.1. Definition

- A *hydrocarbon* is a compound containing only carbon and hydrogen.

XV.13.3.2. Classification

- Aliphatic Hydrocarbons or Chain Compounds.

1. Methane Series (Alkanes) (Paraffins), C_nH_{2n+2}.

(a) The members of this series contain only carbon atoms joined by single valence bonds.

(b) These hydrocarbons are found principally in natural gas and petroleum.

(c) Methane (Fire Damp, or Marsh Gas), CH_4.

1°- Natural gas contains as high as 90% of methane

2°- It may be prepared by heating sodium acetate and soda lime (NaOH and CaO)

$$CH_3COONa + NaOH \xrightarrow{\Delta} Na_2CO_3 + CH_4$$

3°-Methane is a colorless, odorless, inactive gas, and only slightly soluble in water

4°- It burns in air and forms explosive mixtures with air

5°- It is used principally as a fuel.

(d) Other members are ethane, C_2H_6; propane, C_3H_8; butane C_4H_{10}; etc.

(e) These hydrocarbons in petroleum supply naphtas, gasoline, kerosene, lubricating oils, vaseline, paraffin, etc.

2. Ethylene Series (Alkenes) (Olefines), C_nH_{2n}.

(a) The members of this series contain two carbon atoms joined by a double valence bond.

(b) Ethylene, C_2H_4, or $H_2C = CH_2$, is the first member of the series.

1°- Ethylene can be prepared by the action of sulfuric acid on ethyl alcohol.

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$$C_2H_5OH + (H_2SO_4) \rightarrow C_2H_4 + H_2O + (H_2SO_4)$$

(c) The alkenes form numerous addition compounds with Br_2, Cl_2, I_2, O_3, H_2, HCl, HBr, HI, H_2SO_4, etc.

$$H_2C = CH_2 + Br_2 \rightarrow H_2BrC \text{ — } CH_2Br$$

3. Acetylene Series (Alkynes) (Olefines), C_nH_{2n-2}.

(a) The members of this series contain two carbon atoms joined by a triple valence bond.

(b) Acetylene, C_2H_2, or $HC \equiv CH$.

1°- Acetylene is prepared by the action of water on calcium carbide.

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

2°- Acetylene is a colorless, explosive gas, slightly soluble in water, but very soluble in acetone under pressure.

3°- Acetylene burns in air producing a brilliant white light.

4°- It has the ability to form numerous addition compounds.

$$HC \equiv CH + 2\ Cl_2 \rightarrow HCl_2C \text{ — } CHCl_2$$

5°- Acetylene is used for light and in the oxy-acetylene torch.

- Aromatic Hydrocarbons or Ring Compounds.

1. Benzene Series, C_nH_{2n-6}.

(a) The members of this series contain a carbon ring of six carbon atoms with alternate double valence bonds.

(b) These hydrocarbons are obtained principally from the fractional distillation of coal tar.

(c) Benzene, C_6H_6, is the first and most important member of the series.

1°- Benzene is a colorless liquid, insoluble in water, with a boiling point of 80.08°C, and a melting point of 5.48°C.

2°- Benzene burns in air witha smoky flame.

3°- It enters into numerous replacement reactions.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 \text{ (Nitrobenzene) } + H_2O$$

4°- Benzene enters into numerous addition reactions.

$$C_6H_6 + 3\ H_2 \rightarrow C_6H_{12}$$

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5°- Benzene is an important solvent and is used in the preparation of numerous "coal tar" dyes and other organic compounds.

(d) Toluene, $C_6H_5CH_3$, is the second member of the benzene series.

1°- It is obtained from coal tar and crude oil.

2°- Its chemical properties are similar to those of benzene.

3°- It is used in the preparation of numerous dyes, organic compounds, and explosives (T.N.T., Trinitrotoluene).

2. Other aromatic series are those of Naphthalene, C_nH_{2n-12}, and Anthracene, C_nH_{2n-18}.

XV.13.4. Derivatives of hydrocarbons

XV.13.4.1. Halogen Substitution Products

- Halogen substitution products are formed by the substitution of halogen atoms for one or more of the hydrogen atoms in hydrocabons
- Examples.

1. CH_4, Methane.

(a) CH_3I, monoiodomethane, or methyl iodide.

(b) CHI_3, triiodomethane, or iodoform.

(c) CCl_4, tetraclormethane, or carbon tetrachloride. (See § XV.27.)

(b) $CHCl_3$, trichloromethane, or chloroform.

1°- This compound is prepared by the action of bleaching powder on alcohol or acetone.

2°- Chloroform is a heavy, colorless, non-inflammable liquid, with a sweet odor.

3°- It is used as an anasthetic and solvent.

XV.13.4.2. Alcohols

- Alcohols are hydrocarbons in which one or more hydrogen atoms have been replaced by hydroxyl groups (OH).

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- Alcohols containing one (OH) group are known as *monohydroxy* alcohols, with two (OH) groups as *dihydroxy* alcohols, and with three (OH) groups as *trihydroxy* alcohols, etc.
    1. Monohydroxy alcohols have the general formula, ROH, where R has the general formula (C_nH_{2n+1}), and is known as the alkyl group.
    2. Monohydroxy alcohols are named from the corresponding hydrocarbons.
    3. These same alkyl groups appear in numerous other organic compounds.
- Examples.
    1. Methanol (Methyl Alcohol) (Wood Alcohol), CH_3OH.
        (a) Methanol was formerly made by the destructive distillation of wood, hence its name, "wood alcohol.".
        (b) Today it is prepared by the action of carbon monoxide and hydrogen in the presence of a catalyst.

$$CO + 2\ H_2 \rightarrow CH_3OH$$

        (c) Methanol is a colorless, poisonous, liquid with a characteristic color, and is miscible with water in all proportions.
        (d) It can readily be converted to formaldehyde or esters.
        (e) It is used as a solvent for varnishes and shellacs, for a fuel, in denaturing ethyl alcohol, in making formaldehyde, and as an anti-freeze for automobile radiators.
    2. Ethanol (Ethyl Alcohol) (Grain Alcohol), C_2H_5OH.
        (a) Ethanol is prepared by the fermentation of sugars.

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

        (b) Ethanol is a colorless liquid, miscible with water in all proportions.
        (c) It burns in air, reacts with sodium, and forms esters.

$$C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$$

$$2\ C_2H_5OH + 2\ Na \rightarrow 2\ C_2H_5ONa + H_2$$

$$C_2H_5OH + CH_3COOH \rightarrow 2\ CH_3COOC_2H_5 + H_2O$$

        (d) It is used in organic synthesis, beverages, patent medicines, as a solvent, fuel, in the preparation of ether and chloroform, and as an anti-freeze for automobile radiators.
        (e) Denaturated alcohol is alcohol to which poisonous or objectionable adulterants have added to render it unfit for beverage purposes.
    3. Butanol (Butyl Alcohol), C_4H_9OH.
        (a) Butanol is prepared principally by the fermentation of starch in corn.

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(b) It is used principally as a solvent in the manufacture of lacquers.

4. Ethanediol (Ethylene Alcohol) (Glycol) (Prestone), $C_2H_4(OH)_2$.

   (a) It is a typical example of a dihydroxy alcohol and is used extensively as an anti-freeze for automobile radiators.

5. Glycerol (Glycerine), $C_3H_5(OH)_3$.

   (a) Glycerol is the most example of a trihydroxy alcohol.

   (b) It is obtained as a by-product in the manufacture of soap, and in 25% yield by the fermentation of glucose.

   (c) Glycerine is a heavy, sweet, hygroscopic, high boiling, syrupy liquid, soluble in water in all proportions.

   (d) It is used in making anti-freeze automobile solutions, pharmaceuticals, and explosives (nitroglycerine and dynamite).

6. Phenol (Carbolic Acid), C_6H_5OH.

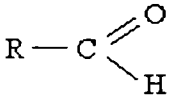
   (a) Phenol is obtained from coal tar.

   (b) It is extremely corrosive to flesh, and is poisonous.

   (c) It is used in making synthetic resins, plastics, and explosives (picric acid).

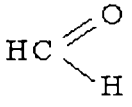
XV.13.4.3. Aldehydes

- Aldehydes are formed by the substitution of an atom for two hydrogen atoms on a terminal carbon atom of a hydrocabon chain.



- They have the general formula,

- Examples.



1. Formaldehyde (Methanal) (Formalin),

   (a) Formaldehyde is prepared by the oxidation of methanol over copper gauze

$$2\ CH_3OH + O_2 \rightarrow 2\ HCHO + 2\ H_2O$$

   (b) It is a colorless gas with a sharp odor, soluble in water, and chemically active.

   (c) It is used as a germicide, preservative, disinfectant and in the preparation of synthetic resins (Bakelite).

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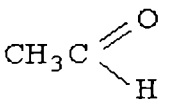

2. Acetaldehyde (Ethanal),

(a) Acetaldehyde is prepared by the hydrolysis of acetylene or by the oxidation of ethanol.

(b) It is used in synthetic organic preparations.

XV.13.4.4. Ketones

- Ketones have the general formula, $R_2C = O$.
- Acetone (Dimethyl ketone) is the most imporatnt.
  1. Acetone may be prepared by the fermentation of starch in corn, the destructive distillation of wood, or by heating calcium acetate.

$$(CH_3COO)_2Ca \xrightarrow{\Delta} CaCO_3 + (CH_3)_2C = O$$

  2. Acetone is a colorless, low-boiling liquid that is miscible with water in all proportions.
  3. It is used extensively as a solvent, in the manufacture of chloroform, lacquers, and explosives.

XV.13.4.5. Organic Acids

- Mono-basic organic acids have the general formula, RCOOH.
  1. The "COOH" group is known as a carboxyl group.
- Acids containing two (COOH) groups are known as dibasic acids, three (COOH) groups as tribasic acids, etc.
- Examples.
  1. Formic Acid (Methanoic Acid), HCOOH.
     (a) Formic acid is a colorless, hygroscopic liquid with a pungent, irritating odor.
     (b) Formic acid is corrosive and irritating to the skin and is present in the bite and sting of many insects.
  2. Acetic Acid (Ethanoic Acid), CH_3COOH.

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(a) Acetic acid is formed by the oxidation of ethanol and by the destructive distillation of wood.

(b) Acetic acid is a colorless liquid with a sharp penetrating odor and a sour taste, and soluble in water.

(c) Acetic acid is used in making vinegar, white lead, esters and dyes.

3. Other common organic acids.

(a) Oxalic acid, $(COOH)_2$, a solid, is used in ink eradicators, as a bleach, for cleaning metals, and in dyeing and tanning.

(b) Tartaric acid (the acid of grapes), $H_2(C_4H_4O_6)$, a solid, is used in soft drinks, baking powder, and the dye industry.

(c) Citric acid (the acid of citrus fruits), $H_3(C_6H_5O_7)$, a solid, is used in soft drinks, medicine, and dye industry.

XV.13.4.6. Esters

- Esters are essentially organic salts, formed from the reaction of organic acids with alcohols.
- They have the general formula, RCOOR'.
- Many esters have pleasant odors and tastes and are used in extracts and perfumes.
- Examples.

1. Ethyl Acetate, $CH_3COOC_2H_5$.

(a) This ester is prepared by the action of ethyl alcohol on acetic acid. (Esterification.)

$$C_2H_5OH + CH_3COOH \rightarrow 2\ CH_3COOC_2H_5 + H_2O$$

(b) Ethyl acetate is used as a solvent and in artificial flavors.

XV.13.4.7. Ethers

- An ether is an organic oxide with the general formula, ROR.
- Diethyl ether, $C_2H_5 — O — C_2H_5$, is the most common and important ether.

1. It is prepared by the action of sulfuric acid on ethyl alcohol.

$$2\ C_2H_5OH + (H_2SO_4) \rightarrow C_2H_5 — O — C_2H_5 + H_2O + (H_2SO_4)$$

2. Ether is a light, volatile, inflammable liquid.
3. It is used as a solvent for fats and as an anaesthetic.

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XV.13.4.8. Fats

- Fats are glyceryl, fatty acid esters of plant and animal origin.
- Examples.
    1. Stearin, $C_3H_5(C_{17}H_{35}COO)_3$, from beef tallow.
    2. Palmitin, $C_3H_5(C_{15}H_{31}COO)_3$, from beef and mutton fat.
    3. Olein, $C_3H_5(C_{17}H_{33}COO)_3$, from linseed and olive oil.
- Fats are used principally for foods and soap manufacture.
- Hydrogenated cottonseed oil (Crisco) is used as a lard substitute.

XV.13.4.9. Soaps

- Soap are sodium and potassium salts of fatty acids.
- They are prepared by heating a fat with sodium hydroxide.

$$(C_{17}H_{35}COO)_3C_3H_5 \text{ (Fat)} + 3\ NaOH \rightarrow C_3H_5(OH)_3 \text{ (Glycerol)} + 3\ C_{17}H_{35}COONa \text{ (Soap)}$$

- Soap Owes its cleaning power to its ability to emulsify fats and dirt with water.

XV.13.5. Carbohydrates

XV.13.5.1. Definition

- Carbohydrates are polyhydroxy aldehydes, or polyhydroxy ketones, or compounds which yield these substances on hydrolysis.
- Most "carbohydrates" imply "hydrates of carbon." or contain hydrogen and oxygen in the ratio of 2 to 1, in combination with carbon.

XV.13.5.2. Types of Carbohydrates

- Monosaccharides (Simple Sugars).
    1. Glucose (Dextrose), $C_6H_{12}O_6$,

        (a) Glucose is found in fruit and honey.
        (b) It is produced commercially by the hydrolysis of cane sugar or starch.
        (c) Glucose is a sweet, soluble, crystalline, optically active sugar.
        (d) It reduces Fehling's solution and is fermentable.
        (e) It is produced for making jellies, candies, and other food products.

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- Disaccharides. (Yield two simple sugars on hydrolysis.)

  1. Sucrose (Cane of Beet Sugar), $C_{12}H_{22}O_{11}$,

     (a) It is prepared from sugar cane, sugar beets, and the sap of maple trees.

     (b) Sucrose is a sweet, soluble, crystalline, optically active sugar.

     (c) On hydrolysis it yields equal molecular concentrations of glucose and fructose.

     $$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 \text{ (Glucose)} + C_6H_{12}O_6 \text{ (Fructose)}$$

     (d) Sucrose is the most important commercial sugar and is used to sweeten and preserve food.

- Polysaccharides. (Yield several simple sugars on hydrolysis.)

  1. Starch, $(C_6H_{10}O_5)n$.

     (a) Starch is found in numerous plants, grains and potatoes being important sources.

     (b) Starch is an insoluble, white, powdery solid and forms colloidal dispersions.

     (c) It gives a blue color with iodine and is readily hydrolyzed to glucose.

     $$(C_6H_{10}O_5)n + n\ H_2O \rightarrow n\ C_6H_{12}O_6 \text{ (Glucose)}$$

     (d) Starch is used for food, laundering, and the manufacture of glucose.

  2. Cellulose, $(C_6H_{10}O_5)x$.

     (a) Wood fiber, cotton, straw and hemp are important sources of cellulose.

     (b) Cellulose is a white insoluble solid.

     (c) It reacts with nitric acid forming explosives (gun cotton), and is hydrolyzed with acids.

     (d) It is used for the manufacture of paper and rayon.

XV.13.6. Proteins

XV.13..6.1. Definition

- *Proteins* are complex, high molecular weight compounds, containing C, H, O, and N, and frequently P and S.
- Proteins yield amino acids on hydrolysis.

XV.13.6.2. Occurrence and Properties

- Proteins occur in plant and animal tissues.

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- Lean meats, eggs, peas, beans, and cheese are rich in proteins.
- Albumins, Globulins, and Glutenins are important proteins.
- They are an essential animal food.
- They yield numerous amino acids on hydrolysis, *e.g.*, CH_2NH_2COOH, Glycine.

XV.13.7. Foods

XV.13.7.1. Definition

- A *food* is a substance that may be utilized by the animal body to provide necessary material for growth, energy and warmth without producing objectionable by-products.

XV.13.7.2. Classification of Foods

- *Carbohydrates* are oxidized to carbon dioxide and water.
- *Fats* are oxidized also to carbon dioxide and water.
- *Proteins* build tissues and yield the same products on oxidation, and in addition nitrogenous compounds such as urea, uric acid, and creatinine.
- *Minerals* are important constituents of bones, blood and teeth, and tend to regulate numerous body activities.
- *Water* maintains the necessary colloidal condition of the body and compensates for loss through perspiration and the urine.
- *Oxygen* is necessary for the oxidation of foods resulting in the libaration of heat and energy.
    1. The energy of food can be measured with a calorimeter and expressed in calories.
    2. A normal adult requires from 2000 to 5000 large calories of food energy per day.
- *Vitamins* are auxiliary, complex food products that maintain proper growth, health, and the prevention of disease.
    1. *Vitamin A* is fat soluble and promotes growth in children. It is found in cod-liver oil, butter, cream, and green leafy vegetables.
    2. *Vitamin B* is water soluble and prevents the disease, beri-beri. It is found yeast, nuts, citrus fruits, and some vegetables.
    3. *Vitamin C* is water soluble and prevents scuvy. It is found in citrus fruits, tomatoes, milk, and fresh vegetables.

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4. *Vitamin D* is fat soluble and prevents rickets. It is found in cod-liver oil, spinach, and other green vegetables. The vitamin D content of milk is increased by irradiation with ultra violet light.
5. *Vitamin E* is also fat soluble and prevents sterility in animals. It is found in wheat germs and lettuce.
6. *Vitamin G* prevents pellagra. It is found in milk, fruits and vegetables.
7. Other vitamins recently reported include H, K, and P with several subclassifications of many.

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